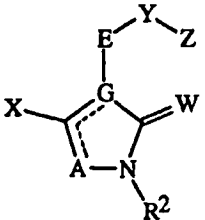




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07D 405/04, A01N 43/647, C07D 409/04, 401/04, 249/12, 261/12, 413/04, 417/14	A1	(11) International Publication Number: WO 96/36633 (43) International Publication Date: 21 November 1996 (21.11.96)
(21) International Application Number: PCT/US96/06533 (22) International Filing Date: 8 May 1996 (08.05.96) (30) Priority Data: 08/443,295 17 May 1995 (17.05.95) US (60) Parent Application or Grant (63) Related by Continuation US 08/443,295 (CIP) Filed on 17 May 1995 (17.05.95) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BROWN, Richard, James [US/US]; 225 North Star Road, Newark, DE 19711-2939 (US). DANIEL, Dilon, Jancey [GD/US]; 3407 Christiana Meadows, Bear, DE 19701-2867 (US). FRASIER, Deborah, Ann [US/US]; 2371 Pinnacle Drive, Martinez, CA 94553-5029 (US). HOWARD, Michael, Henry, Jr. [US/US]; P.O. Box 407, 908 Montchanin Road, Rockland, DE 19732-0407		(US). KOETHER, Gerard, Michael [US/US]; 2304 Porter Road, Bear, DE 19701-2021 (US). RORER, Morris, Padgett [US/US]; 64 Lower Valley Lane, Newark, DE 19711-6719 (US). (74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FUNGICIDAL CYCLIC AMIDES		
(57) Abstract <p>Compounds of Formula (I), and their N-oxides and agriculturally suitable salts, are disclosed which are useful as fungicides. In said formula, E is a ring system selected from certain 5- to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, or an optionally substituted naphthalene ring as defined in the disclosure; A is O; S; N; NR⁵; or CR¹⁴; G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A; W is O; S; NH; N(C₁-C₆ alkyl); or NO(C₁-C₆ alkyl); X is OR¹; S(O)_mR¹; or halogen; R¹ is C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxy carbonyl; R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxy carbonyl; hydroxy; C₁-C₂ alkoxy; or acetyloxy; R⁵ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxy carbonyl; and Y, Z, R¹⁴ and m are as defined in the disclosure. Also disclosed are compositions containing the compounds of Formula (I) and a method for controlling plant diseases caused by fungal plant pathogens which involves applying an effective amount of a compound of Formula (I).</p> <div style="text-align: right;">  <p style="text-align: right;">(I)</p> </div>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE

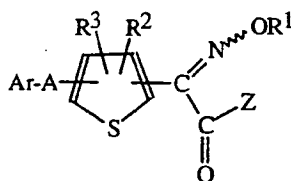
FUNGICIDAL CYCLIC AMIDES

BACKGROUND OF THE INVENTION

This invention relates to certain cyclic amides, their *N*-oxides, agriculturally suitable salts and compositions, and methods of their use as fungicides.

The control of plant diseases caused by fungal plant pathogens is extremely important in achieving high crop efficiency. Plant disease damage to ornamental, vegetable, field, cereal, and fruit crops can cause significant reduction in productivity and thereby result in increased costs to the consumer. Many products are commercially available for these purposes, but the need continues for new compounds which are more effective, less costly, less toxic, environmentally safer or have different modes of action.

WO 95/01973 discloses certain heterocyclic amides and esters of Formula i as fungicides



i

15

wherein

Ar is substituted aryl or heteroaryl;

R¹ is alkyl or haloalkyl;

R² and R³ are independently, among others, hydrogen, halogen, cyano, nitro, alkyl, alkoxy, alkylthio, alkenyl, alkenyloxy, alkynyl, alkynyloxy, haloalkyl, haloalkoxy, haloalkenyl, haloalkynyl, alkoxycarbonyl, or substituted phenyl;

A is -O-; -CH=CH-; -C≡C-; -CH₂O-; -OCH₂-; -CH₂S(O)_n-; -S(O)_nCH₂-; -S(O)_n-; -C(R⁴)=N-O-; -C(R⁴)=N-OCH₂-; or -NR⁶-;

Z is OR⁵ or NR⁶R⁷;

R⁴ is H, alkyl, haloalkyl, cycloalkyl or cyano;

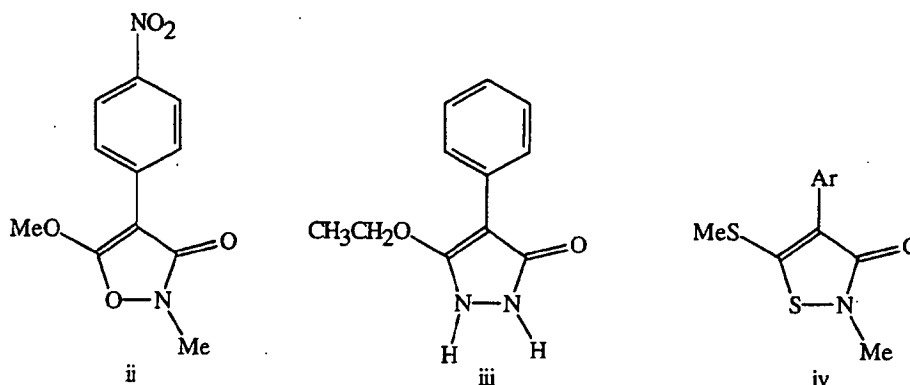
R⁵ is alkyl or haloalkyl;

R⁶ and R⁷ are independently H, alkyl, haloalkyl or alkoxy; and

n is 0, 1 or 2.

The cyclic amides of the present invention are not disclosed therein.

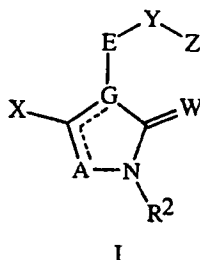
J. Heterocyclic Chem., (1987), 24, 465, *J. Heterocyclic Chem.*, (1988), 25, 1307, and *Australian J. Chem.*, (1977), 30 (8), 1815 disclose 4-nitrophenyl isoxazoles (ii), phenyl pyrazolones (iii), and aryl isothiazolinones (iv) respectively.



However, no utility as fungicides is alleged and the cyclic amides of the present invention are not disclosed therein.

SUMMARY OF THE INVENTION

This invention is directed to compounds of Formula I including all geometric and stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural compositions containing them and their use as fungicides:



wherein

E is a ring system selected from:

- i) 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes

- one or two Q as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with one of R³, R⁴, or both R³ and R⁴; and
- 5 ii) a naphthalene ring, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalene ring optionally substituted with one of R³, R⁴, or both R³ and R⁴, provided that when G is attached to the 1, 4, 5, or 8 position of the naphthalene ring and Z is C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl or phenyl each substituted with R⁹ and optionally substituted with one or more R¹⁰, then Y is other than -O-, -S(O)_n-, -C(=O)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C≡C-, -OCHR¹⁵-, -S(O)_nCHR¹⁵- or a direct bond;
- 10 A is O; S; N; NR⁵; or CR¹⁴;
- 15 G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;
- W is O; S; NH; N(C₁-C₆ alkyl); or NO(C₁-C₆ alkyl);
- 20 X is OR¹; S(O)_mR¹; or halogen;
- R¹ is C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxycarbonyl;
- 25 R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxycarbonyl; hydroxy; C₁-C₂ alkoxy; or acetyloxy;
- 30 R³ and R⁴ are each independently halogen; cyano; nitro; hydroxy; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyloxy; C₂-C₆ alkynyloxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; formyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl; NH₂C(O); (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); Si(R²⁵)₃; Ge(R²⁵)₃; (R²⁵)₃Si-C≡C-; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R⁸ and optionally substituted with one or more R¹⁰;

R^5 is H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_2 - C_6 haloalkynyl; C_3 - C_6 cycloalkyl; C_2 - C_4 alkylcarbonyl; or C_2 - C_4 alkoxycarbonyl;

Y is -O-; -S(O)_n-; -NR¹⁵-; -C(=O)-; -CH(OR¹⁵)-; -CHR⁶-; -CHR⁶CHR⁶-;
 5 -CR⁶=CR⁶-; -C≡C-; -CHR¹⁵O-; -OCHR¹⁵-; -CHR¹⁵S(O)_n-; -S(O)_nCHR¹⁵-;
 -CHR¹⁵O-N=C(R⁷)-; -(R⁷)C=N-OCH(R¹⁵)-; -C(R⁷)=N-O-; -O-N=C(R⁷)-;
 -CHR¹⁵OC(=O)N(R¹⁵)-; -CHR¹⁵OC(=S)N(R¹⁵)-; -CHR¹⁵OC(=O)O-;
 -CHR¹⁵OC(=S)O-; -CHR¹⁵OC(=O)S-; -CHR¹⁵OC(=S)S-;
 -CHR¹⁵SC(=O)N(R¹⁵)-; -CHR¹⁵SC(=S)N(R¹⁵)-; -CHR¹⁵SC(=O)O-;
 10 -CHR¹⁵SC(=S)O-; -CHR¹⁵SC(=O)S-; -CHR¹⁵SC(=S)S-;
 -CHR¹⁵SC(=NR¹⁵)S-; -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-;
 -CHR¹⁵O-N(R¹⁵)C(=O)N(R¹⁵)-; -CHR¹⁵O-N(R¹⁵)C(=S)N(R¹⁵)-;
 -CHR¹⁵O-N=C(R⁷)NR¹⁵-; -CHR¹⁵O-N=C(R⁷)OCH₂-;
 -CHR¹⁵O-N=C(R⁷)-N=N-; -CHR¹⁵O-N=C(R⁷)-C(=O)-;
 15 -CHR¹⁵O-N=C(R⁷)-C(=N-A²-Z¹)-A¹-;
 -CHR¹⁵O-N=C(R⁷)-C(R⁷)=N-A²-A³-; -CHR¹⁵O-N=C(-C(R⁷)=N-A²-Z¹)-;
 -CHR¹⁵O-N=C(R⁷)-CH₂O-; -CHR¹⁵O-N=C(R⁷)-CH₂S-;
 -O-CH₂CH₂O-N=C(R⁷)-; -CHR¹⁵O-C(R¹⁵)=C(R⁷)-; -CHR¹⁵O-C(R⁷)=N-;
 -CHR¹⁵S-C(R⁷)=N-; -C(R⁷)=N-NR¹⁵-; -CH=N-N=C(R⁷)-;
 20 -CHR¹⁵N(R¹⁵)-N=C(R⁷)-; -CHR¹⁵N(COCH₃)-N=C(R⁷)-;
 -OC(=S)NR¹⁵C(=O)-; -CHR⁶-C(=W¹)-A¹-; -CHR⁶CHR⁶-C(=W¹)-A¹-;
 -CR⁶=CR⁶-C(=W¹)-A¹-; -C≡C-C(=W¹)-A¹-; -N=CR⁶-C(=W¹)-A¹-; or a
 direct bond; and the directionality of the Y linkage is defined such that the
 moiety depicted on the left side of the linkage is bonded to E and the moiety
 25 on the right side of the linkage is bonded to Z;

Z¹ is H or -A³-Z;

W¹ is O or S;

A¹ is O; S; NR¹⁵; or a direct bond;

A² is O; NR¹⁵; or a direct bond;

30 A³ is -C(=O)-; -S(O)₂-; or a direct bond;

each R⁶ is independently H; 1-2 CH₃; C_2 - C_3 alkyl; C_1 - C_3 alkoxy; C_3 - C_6
 cycloalkyl; formylamino; C_2 - C_4 alkylcarbonylamino; C_2 - C_4
 alkoxycarbonylamino; NH₂C(O)NH; (C_1 - C_3 alkyl)NHC(O)NH;
 (C_1 - C_3 alkyl)₂NC(O)NH; N(C_1 - C_3 alkyl)₂; piperidiny; morpholiny;
 35 1-2 halogen; cyano; or nitro;

each R⁷ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; C₁-C₆ haloalkylthio; C₁-C₆ haloalkylsulfinyl; C₁-C₆ haloalkylsulfonyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxy carbonyl; halogen; cyano; nitro; hydroxy; amino; NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; or morpholinyl;

each Z is independently selected from:

- i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, and C₂-C₁₀ alkynyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;
- ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R⁹ and optionally substituted with one or more R¹⁰;
- iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each nonaromatic or aromatic heterocyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰;
- iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from C(=O) and S(O)₂, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R⁹ and optionally substituted with one or more R¹⁰; and
- v) adamantyl substituted with R⁹ and optionally substituted with one or more R¹⁰;

each Q is independently selected from the group -CHR¹³-, -NR¹³-, -O-, and -S(O)_p-;

R⁸ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl;

- C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy; CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; cyano; nitro; SiR¹⁹R²⁰R²¹; or GeR¹⁹R²⁰R²¹;
- R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₁-C₆ alkylthio; C₁-C₆ haloalkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl; C₃-C₆ alkenyloxy; CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; -C(R¹⁸)=NOR¹⁷; cyano; nitro; SF₅; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R¹¹, R¹², or both R¹¹ and R¹²;
- each R¹⁰ is independently halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₁-C₄ alkoxy; nitro; or cyano; or
- when R⁹ and an R¹⁰ are attached to adjacent atoms on Z, R⁹ and said adjacently attached R¹⁰ can be taken together as -OCH₂O- or -OCH₂CH₂O-; each CH₂ group of said taken together R⁹ and R¹⁰ optionally substituted with 1-2 halogen; or
- when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is
- CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -O-CH₂CH₂O-N=C(R⁷)-, -CHR¹⁵O-C(R¹⁵)=C(R⁷)-, -CH=N-N=C(R⁷)-, -CHR¹⁵N(R¹⁵)-N=C(R⁷)- or -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z;
- J is -CH₂-; -CH₂CH₂-; -OCH₂-; -CH₂O-; -SCH₂-; -CH₂S-; -N(R¹⁶)CH₂-; or -CH₂N(R¹⁶)-; each CH₂ group of said J optionally substituted with 1 to 2 CH₃;
- R¹¹ and R¹² are each independently halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₁-C₄ alkoxy; C₁-C₄ haloalkoxy; nitro; cyano; Si(R²⁵)₃; or Ge(R²⁵)₃;
- each R¹³ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- R¹⁴ is H; halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; or C₃-C₆ cycloalkyl;
- each R¹⁵ is independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; or
- when Y is -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-, the two R¹⁵ attached to nitrogen atoms on said group can be taken together as -(CH₂)_s-; or

when Y is $-\text{CHR}^{15}\text{O}-\text{N}=\text{C}(\text{R}^7)\text{NR}^{15}-$, R^7 and the adjacently attached R^{15} can be taken together as $-\text{CH}_2-(\text{CH}_2)_s-$; $-\text{O}-(\text{CH}_2)_s-$; $-\text{S}-(\text{CH}_2)_s-$; or $-\text{N}(\text{C}_1-\text{C}_3 \text{ alkyl})-(\text{CH}_2)_s-$; with the directionality of said linkage defined such that the moiety depicted on the left side of the linkage is bonded to the carbon and the moiety on the right side of the linkage is bonded to the nitrogen;

R^{16} , R^{17} , and R^{18} are each independently H; C_1-C_3 alkyl; C_3-C_6 cycloalkyl; or phenyl optionally substituted with halogen, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, nitro or cyano;

R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , and R^{24} are each independently C_1-C_6 alkyl; C_2-C_6 alkenyl; C_1-C_4 alkoxy; or phenyl;

each R^{25} is independently C_1-C_4 alkyl; C_1-C_4 haloalkyl; C_2-C_4 alkenyl; C_1-C_4 alkoxy; or phenyl;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

s is 2 or 3.

DETAILS OF THE INVENTION

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. The term "1-2 CH_3 " indicates that the substituent can be methyl or, when there is a hydrogen attached to the same atom, the substituent and said hydrogen can both be methyl.

"Alkenyl" includes straight-chain or branched alkenes such as vinyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also

includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl. "Alkoxy" includes, for

example, methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkenyloxy" includes straight-chain or branched alkenyloxy

moieties. Examples of "alkenyloxy" include $\text{H}_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}$. "Alkynyloxy" includes straight-chain or branched alkynyloxy moieties. Examples of "alkynyloxy"

include $\text{HC}\equiv\text{CCH}_2\text{O}$, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$ and $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$. "Alkylthio" includes

branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylsulfinyl" includes

both enantiomers of an alkylsulfinyl group. Examples of "alkylsulfinyl" include $\text{CH}_3\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})$, $(\text{CH}_3)_2\text{CHS}(\text{O})$ and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of "alkylsulfonyl" include $\text{CH}_3\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$, $(\text{CH}_3)_2\text{CHS}(\text{O})_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. "Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. "Cycloalkenyl" includes groups such as cyclopentenyl and cyclohexenyl as well as groups with more than one double bond such as 1,3- and 1,4-cyclohexadienyl. The term "aromatic carbocyclic ring system" includes fully aromatic carbocycles and carbocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). The term "nonaromatic carbocyclic ring system" denotes fully saturated carbocycles as well as partially or fully unsaturated carbocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The term "aromatic heterocyclic ring system" includes fully aromatic heterocycles and heterocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). The term "nonaromatic heterocyclic ring system" denotes fully saturated heterocycles as well as partially or fully unsaturated heterocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The heterocyclic ring systems can be attached through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen. One skilled in the art will appreciate that not all nitrogen containing heterocycles can form *N*-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen containing heterocycles which can form *N*-oxides.

The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. The term "1-2 halogen" indicates that one or two of the available positions for that substituent may be halogen which are independently selected. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C , ClCH_2 , CF_3CH_2 and CF_3CCl_2 . The terms "haloalkenyl", "haloalkynyl", "haloalkoxy", and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include $(\text{Cl})_2\text{C}=\text{CHCH}_2$ and $\text{CF}_3\text{CH}_2\text{CH}=\text{CHCH}_2$. Examples of "haloalkynyl" include $\text{HC}\equiv\text{CCHCl}$, $\text{CF}_3\text{C}\equiv\text{C}$, $\text{CCl}_3\text{C}\equiv\text{C}$ and $\text{FCH}_2\text{C}\equiv\text{CCH}_2$. Examples of "haloalkoxy" include CF_3O , $\text{CCl}_3\text{CH}_2\text{O}$, $\text{HCF}_2\text{CH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{O}$. Examples of "haloalkylthio" include CCl_3S , CF_3S , $\text{CCl}_3\text{CH}_2\text{S}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{S}$. Examples of "haloalkylsulfinyl" include $\text{CF}_3\text{S}(\text{O})$,

$\text{CCl}_3\text{S}(\text{O})$, $\text{CF}_3\text{CH}_2\text{S}(\text{O})$ and $\text{CF}_3\text{CF}_2\text{S}(\text{O})$. Examples of "haloalkylsulfonyl" include $\text{CF}_3\text{S}(\text{O})_2$, $\text{CCl}_3\text{S}(\text{O})_2$, $\text{CF}_3\text{CH}_2\text{S}(\text{O})_2$ and $\text{CF}_3\text{CF}_2\text{S}(\text{O})_2$.

The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where i and j are numbers from 1 to 10. For example, $\text{C}_1\text{-C}_3$ alkylsulfonyl designates methylsulfonyl through propylsulfonyl. Examples of "alkylcarbonyl" include $\text{C}(\text{O})\text{CH}_3$, $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$. Examples of "alkoxycarbonyl" include $\text{CH}_3\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OC}(=\text{O})$, $(\text{CH}_3)_2\text{CHOC}(=\text{O})$ and the different butoxy- or pentoxycarbonyl isomers. In the above recitations, when a compound of Formula I is comprised of one or more heterocyclic rings, all substituents are attached to these rings through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

When a group contains a substituent which can be hydrogen, for example R^9 or R^{13} , then, when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I, N -oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

The salts of the compounds of the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds of the invention also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine) or inorganic bases (e.g., hydrides, hydroxides, or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a phenol.

Preferred compounds for reasons of better activity and/or ease of synthesis are:

Preferred 1. Compounds of Formula I above, and N -oxides and agriculturally suitable salts thereof, wherein:

E is selected from the group 1*H*-pyrrole-1,2-, 2,3- and 3,4-diyl; 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl; 1*H*-pyrazole-1,5-, 3,4-

and 4,5-diyl; 1*H*-imidazole-1,2-, 4,5- and 1,5-diyl; 3,4- and 4,5-isoxazolediy; 4,5-oxazolediy; 3,4- and 4,5-isothiazolediy; 4,5-thiazolediy; 1*H*-1,2,3-triazole-1,5- and 4,5-diyl; 2*H*-1,2,3-triazole-4,5-diyl; 1*H*-1,2,4-triazole-1,5-diyl; 4*H*-1,2,4-triazole-3,4-diyl; 1,2,3-oxadiazole-4,5-diyl; 1,2,5-oxadiazole-3,4-diyl; 1,2,3-thiadiazole-4,5-diyl; 1,2,5-thiadiazole-3,4-diyl; 1*H*-tetrazole-1,5-diyl; 2,3- and 3,4-pyridinediy; 3,4- and 4,5-pyridazinediy; 4,5-pyrimidinediy; 2,3-pyrazinediy; 1,2,3-triazine-4,5-diyl; 1,2,4-triazine-5,6-diyl; 1*H*-indole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 1,2-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 2,3-, 4,5-, 5,6- and 6,7-benzofurandiy; benzo[*b*]thiophene-2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 1*H*-indazole-1,4-, 1,5-, 1,6-, 1,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 1*H*-benzimidazole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-diyl; 1,2-benzisoxazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzoxazolediy; 1,2-benzisothiazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzothiazolediy; 2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3-, 3,4-, 5,6-, 6,7- and 7,8-quinolinediy; 1,5-, 1,6-, 1,7-, 1,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-isoquinolinediy; 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and 7,8-cinnolinediy; 1,5-, 1,6-, 1,7-, 1,8-, 5,6-, 6,7- and 7,8-phthalazinediy; 2,5-, 2,6-, 2,7-, 2,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-quinazolinediy; 2,5-, 2,6-, 2,7-, 2,8-, 2,3-, 5,6-, 6,7- and 7,8-quinoxalinediy; 1,8-naphthyridine-2,5-, 2,6-, 2,7-, 3,5-, 3,6-, 4,5-, 2,3- and 3,4-diyl; 2,6-, 2,7-, 4,6-, 4,7-, 6,7-pteridinediy; pyrazolo[5,1-*b*]thiazole-2,6-, 2,7-, 3,6-, 3,7-, 2,3- and 6,7-diyl; thiazolo[2,3-*c*]-1,2,4-triazole-2,5-, 2,6-, 5,6-diyl; 2-oxo-1,3-benzodioxole-4,5- and 5,6-diyl; 1,3-dioxo-1*H*-isoindole-2,4-, 2,5-, 4,5- and 5,6-diyl; 2-oxo-2*H*-1-benzopyran-3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and 7,8-diyl; [1,2,4]triazolo[1,5-*a*]pyridine-2,5-, 2,6-, 2,7-, 2,8-, 5,6-, 6,7- and 7,8-diyl;

3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazine-3,5-, 3,6-, 3,7-, 3,8-,
 5,6-, 6,7- and 7,8-diyl; 2,3-dihydro-2-oxo-3,4-, 3,5-, 3,6-, 3,7-,
 4,5-, 5,6- and 6,7-benzofurandiyl; thieno[3,2-*d*]thiazole-2,5-, 2,6-,
 and 5,6-diyl; 5,6,7,8-tetrahydro-2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-,
 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 2,3- and 3,4-quinolinediyl;
 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazole-2,4-, 2,5-, 2,6-, 2,7-,
 4,5-, 5,6- and 6,7-diyl; 1,3-benzodioxole-2,4-, 2,5-, 4,5- and
 5,6-diyl; 2,3-dihydro-2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-,
 4,5-, 5,6- and 6,7-benzofurandiyl;
 2,3-dihydro-1,4-benzodioxin-2,5-, 2,6-, 2,7-, 2,8-, 5,6- and 6,7-diyl;
 5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-2,4-, 2,5-, 2,6-, 2,7-,
 2,8-, 3,4-, 3,5-, 3,6-, 3,7-, 3,8-, and 2,3-diyl; and 1,5-, 1,6-, 1,7-,
 1,8-, 2,6-, 2,7-, 1,2-, and 2,3-naphthalenediyl; each aromatic ring
 system optionally substituted with one of R³, R⁴, or both R³ and
 R⁴;

W is O;

R¹ is C₁-C₃ alkyl or C₁-C₃ haloalkyl;

R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or C₃-C₆ cycloalkyl;

R³ and R⁴ are each independently halogen; cyano; nitro; C₁-C₆ alkyl;

C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₁-C₆ alkylthio;
 C₁-C₆ alkylsulfonyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl;
 (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); benzoyl; or
 phenylsulfonyl;

Y is -O-; -CH=CH-; -C≡C-; -CH₂O-; -OCH₂-; -CH₂S(O)_{*n*}-;
 -CH₂O-N=C(R⁷)-; -(R⁷)C=N-OCH(R¹⁵)-; -C(R⁷)=N-O-;
 -CH₂OC(O)NH-; -CH₂S-C(R⁷)=N-; -CH=CR⁶-C(=W¹)-A¹-; or a
 direct bond;

R⁷ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ alkylthio;
 C₂-C₆ alkenyl; C₂-C₆ alkynyl; C₃-C₆ cycloalkyl; halogen; or cyano;
 or

when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is
 -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken
 together as -(CH₂)_{*i*}-J- such that J is attached to Z;

Z is selected from the group C₁-C₁₀ alkyl; C₃-C₈ cycloalkyl; phenyl;
 naphthalenyl; anthracenyl; phenanthrenyl; 1*H*-pyrrolyl; furanyl;
 thienyl; 1*H*-pyrazolyl; 1*H*-imidazolyl; isoxazolyl; oxazolyl;

- isothiazolyl; thiazolyl; 1*H*-1,2,3-triazolyl; 2*H*-1,2,3-triazolyl;
 1*H*-1,2,4-triazolyl; 4*H*-1,2,4-triazolyl; 1,2,3-oxadiazolyl;
 1,2,4-oxadiazolyl; 1,2,5-oxadiazolyl; 1,3,4-oxadiazolyl;
 1,2,3-thiadiazolyl; 1,2,4-thiadiazolyl; 1,2,5-thiadiazolyl;
 5 1,3,4-thiadiazolyl; 1*H*-tetrazolyl; 2*H*-tetrazolyl; pyridinyl;
 pyridazinyl; pyrimidinyl; pyrazinyl; 1,3,5-triazinyl; 1,2,4-triazinyl;
 1,2,4,5-tetrazinyl; 1*H*-indolyl; benzofuranyl; benzo[*b*]thiophenyl;
 1*H*-indazolyl; 1*H*-benzimidazolyl; benzoxazolyl; benzothiazolyl;
 quinolinyl; isoquinolinyl; cinnolinyl; phthalazinyl; quinazolinyl;
 10 quinoxalinyl; 1,8-naphthyridinyl; pteridinyl; 2,3-dihydro-1*H*-indenyl;
 1,2,3,4-tetrahydronaphthalenyl;
 6,7,8,9-tetrahydro-5*H*-benzocycloheptenyl;
 5,6,7,8,9,10-hexahydrobenzocyclooctenyl;
 2,3-dihydro-3-oxobenzofuranyl; 1,3-dihydro-1-oxoisobenzofuranyl;
 15 2,3-dihydro-2-oxobenzofuranyl;
 3,4-dihydro-4-oxo-2*H*-1-benzopyranyl;
 3,4-dihydro-1-oxo-1*H*-2-benzopyranyl;
 3,4-dihydro-3-oxo-1*H*-2-benzopyranyl;
 3,4-dihydro-2-oxo-2*H*-1-benzopyranyl; 4-oxo-4*H*-1-benzopyranyl;
 20 2-oxo-2*H*-1-benzopyranyl;
 2,3,4,5-tetrahydro-5-oxo-1-benzoxepinyl;
 2,3,4,5-tetrahydro-2-oxo-1-benzoxepinyl;
 2,3-dihydro-1,3-dioxo-1*H*-isoindolyl;
 1,2,3,4-tetrahydro-1,3-dioxoisoquinolinyl;
 25 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazinyl;
 2-oxo-1,3-benzodioxyl;
 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazolyl; 9*H*-fluorenyl;
 azulenyl; and thiazolo[2,3-*c*]-1,2,4-triazolyl; each group substituted
 with R⁹ and optionally substituted with one or more R¹⁰;
 30 R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆
 haloalkoxy; C₁-C₆ alkylthio; cyano; CO₂(C₁-C₆ alkyl);
 NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; SiR²²R²³R²⁴; or GeR²²R²³R²⁴;
 or R⁹ is C₃-C₆ cycloalkyl, phenyl, phenoxy, pyridinyl, pyridinyloxy,
 pyrimidinyl, or pyrimidinyloxy, each optionally substituted with one
 35 of R¹¹, R¹², or both R¹¹ and R¹²; and
 each R¹⁵ is independently H; C₁-C₃ alkyl; or C₃-C₆ cycloalkyl.

Preferred 2. Compounds of Preferred 1 wherein:

- 5 E is selected from the group 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl; 2,3- and 3,4-pyridinediyl; 4,5-pyrimidinediyl; 2,4-, 2,7-, 3,5-, 2,3-, 4,5-, 5,6- and 6,7-benzofurandiyl; benzo[*b*]thiophene-2,4-, 2,7-, 3,5-, 2,3-, 4,5-, 5,6- and 6,7-diyl; and 1,6-, 1,7-, 1,2-, and 2,3-naphthalenediyl; each aromatic ring system optionally substituted with one of R³, R⁴, or both R³ and R⁴;
- 10 Z is selected from the group phenyl; 1,2,4-thiadiazolyl; pyridinyl; pyrimidinyl; and naphthalenyl; each group substituted with R⁹ and optionally substituted with one or more R¹⁰;
- R⁷ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ alkylthio; C₂-C₆ alkenyl; C₂-C₆ alkynyl; cyclopropyl; halogen; or cyano; or when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken
- 15 together as -(CH₂)_r-J- such that J is attached to Z;
- J is -CH₂- or -CH₂CH₂-; and
- r is 1.

Preferred 3. Compounds of Preferred 2 wherein:

- 20 A is O; N; NR⁵; or CR¹⁴;
- X is OR¹;
- R¹ is C₁-C₃ alkyl;
- R² is H or C₁-C₂ alkyl;
- Y is -O-; -CH=CH-; -CH₂O-; -CH₂O-N=C(R⁷)-; -(R⁷)C=N-OCH(R¹⁵)-; -CH₂OC(=O)NH-; -CH₂S-C(R⁷)=N-; or -CH=CR⁶-C(=W¹)-A¹;
- 25 R⁷ is H; C₁-C₃ alkyl; C₁-C₃ haloalkyl; C₁-C₃ alkoxy; C₁-C₃ alkylthio; or cyclopropyl; and
- each R¹⁵ is independently H; C₁-C₃ alkyl; or cyclopropyl.

Preferred 4. Compounds of Preferred 3 wherein:

- 30 A is O or NR⁵;
- G is C; and
- Y is -O-; -CH₂O-; or -CH₂O-N=C(R⁷)-.

Preferred 5. Compounds of Preferred 4 wherein:

- R¹ is methyl; and
- R² is methyl.

35 Preferred 6. Compounds of Preferred 3 wherein:

- A is N or CR¹⁴;

G is N; and

Y is -O-; -CH₂O-; or -CH₂O-N=C(R⁷)-.

Preferred 7. Compounds of Preferred 6 wherein:

R¹ is methyl; and

5 R² is methyl.

Most preferred are compounds of Preferred 3 selected from the group:

2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3*H*-1,2,4-triazol-3-one;

10 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3*H*-1,2,4-triazol-3-one;

4-[2-[(2,5-dimethylphenoxy)methyl]-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3*H*-1,2,4-triazol-3-one;

15 (1,1-dimethylethyl) 2-chloro-3-[3-(1,5-dihydro-3-methoxy-1-methyl-5-oxo-4*H*-1,2,4-triazol-4-yl)-2-thienyl]-2-propenoate;

4-[2-[[[3-(4-chlorophenyl)-1,2,4-thiadiazol-5-yl]oxy]methyl]-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3*H*-1,2,4-triazol-3-one; and

20 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[3-[4-(trifluoromethyl)phenyl]-1,2,4-thiadiazol-5-yl]oxy]methyl]-3-thienyl]-3*H*-1,2,4-triazol-3-one.

This invention also relates to fungicidal compositions comprising fungicidally effective amounts of the compounds of the invention and at least one of a surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred compounds.

25 This invention also relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the compounds of the invention (e.g., as a composition described herein). The preferred methods of use are those involving the above preferred compounds.

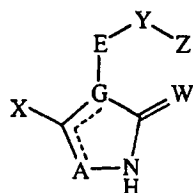
30 Of note are embodiments where E is a naphthalene ring, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalene ring optionally substituted with one of R³, R⁴, or both R³ and R⁴, provided that when G is attached to the 1, 4, 5, or 8 position of the naphthalene ring, then Y is other than -O-, -S(O)_n-, -C(=O)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C≡C-,
35 -OCHR¹⁵-, -S(O)_nCHR¹⁵- or a direct bond; embodiments where R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl,

- C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxy carbonyl; embodiments where Y is -O-, -S(O)_n-, -NR¹⁵-, -C(=O)-, -CH(OR¹⁵)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C≡C-, -CHR¹⁵O-, -OCHR¹⁵-, -CHR¹⁵S(O)_n-, -S(O)_nCHR¹⁵-, -CHR¹⁵O-N=C(R⁷)-, -C(R⁷)=N-OCH(R¹⁵)-, -C(R⁷)=N-O-, -O-N=C(R⁷)-, -CHR¹⁵OC(=O)N(R¹⁵)-,
- 5 -CHR¹⁵OC(=S)N(R¹⁵)-, -CHR¹⁵O-N(R¹⁵)C(=O)N(R¹⁵)-, -CHR¹⁵O-N(R¹⁵)C(=S)N(R¹⁵)-, -CHR¹⁵O-N=C(R⁷)NR¹⁵-, -CHR¹⁵O-N=C(R⁷)OCH₂-, -CHR¹⁵O-N=C(R⁷)-N=N-, -CHR¹⁵O-N=C(R⁷)-C(=O)-, -CHR¹⁵S-C(R⁷)=N-, -C(R⁷)=N-NR¹⁵-, -CH=N-N=C(R⁷)-, -CHR¹⁵N(COCH₃)-N=C(R⁷)-, -OC(=S)NR¹⁵C(=O)-, -CHR⁶-C(=W¹)-A¹-,
- 10 -CHR⁶CHR⁶-C(=W¹)-A¹-, -CR⁶=CR⁶-C(=W¹)-A¹-, -C≡C-C(=W¹)-A¹-, -N=CR⁶-C(=W¹)-A¹- or a direct bond; embodiments where R⁷ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio, C₁-C₆ haloalkylsulfinyl, C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl,
- 15 C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxy carbonyl, halogen, cyano or morpholinyl; embodiments where Z is other than C₃-C₈ cycloalkenyl and adamantyl each substituted with R⁹ and optionally substituted with one or more R¹⁰; embodiments where, when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is -CHR¹⁵O-N=C(R⁷)-, -O-N=C(R⁷)-, -CH=N-N=C(R⁷)- or -CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said
- 20 adjacently attached R¹⁰ are taken together as -(CH₂)_r-J- such that J is attached to Z; embodiments where R¹⁹, R²⁰, R²¹, R²², R²³, and R²⁴ are each independently C₁-C₆ alkyl, C₁-C₄ alkoxy or phenyl; embodiments where each R²⁵ is independently C₁-C₄ alkyl or phenyl; embodiments where R³ and R⁴ are each independently halogen, cyano, nitro, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆
- 25 alkylsulfonyl, C₂-C₆ alkylcarbonyl, C₂-C₆ alkoxy carbonyl, (C₁-C₄ alkyl)NHC(O), (C₁-C₄ alkyl)₂NC(O), benzoyl or phenylsulfonyl; and embodiments where Z is selected from the group phenyl, pyridinyl, pyrimidinyl and naphthalenyl, each group substituted with R⁹ and optionally substituted with one or more R¹⁰.

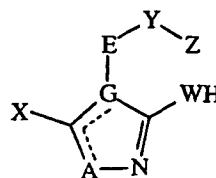
- The compounds of Formula I can be prepared by one or more of the following
- 30 methods and variations as described in Schemes 1-33. The definitions of E, A, G, W, X, R¹-R²⁵, Y, Z¹, W¹, A¹-A³, Z, Q, J, m, n, p, r and s in the compounds of Formulae 1-58 below are as defined above in the Summary of the Invention. Compounds of Formulae Ia-Io are various subsets of the compounds of Formula I, and all substituents for Formulae Ia-Io are as defined above for Formula I.

- 35 One skilled in the art will recognize that some compounds of Formula I can exist in one or more tautomeric forms. For example, a compound of Formula I wherein R² is H

may exist as tautomer Ia or Ib, or both Ia and Ib. The present invention comprises all tautomeric forms of compounds of Formula I.



Ia



Ib

5

The compounds of Formula I can be prepared as described below in Procedures 1) to 5). Procedures 1) to 4) describe syntheses involving construction of the amide ring after the formation of the aryl moiety (E-Y-Z). Procedure 5) describes syntheses of the aryl moiety (E-Y-Z) with the amide ring already in place.

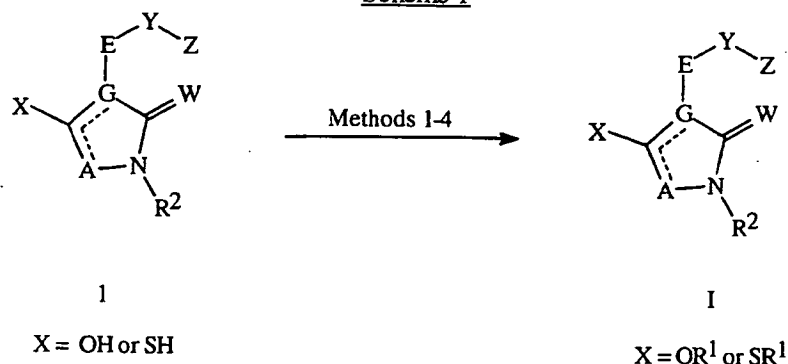
10 1) Alkylation Procedures

The compounds of Formula I are prepared by treating compounds of Formula 1 with an appropriate alkyl transfer reagent in an inert solvent with or without additional acidic or basic reagents or other reagents (Scheme 1). Suitable solvents are selected from the group consisting of polar aprotic solvents such as acetonitrile, dimethylformamide or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; and halocarbons such as dichloromethane or chloroform.

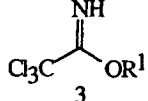
15

17

Scheme 1



Method 1: U-CH=N_2 (U = H or $(\text{CH}_3)_3\text{Si}$)
2

Method 2:  ; Lewis acid
3

Method 3: $(\text{R}^1)_3\text{O}^+ \text{BF}_4^-$
4

Method 4: $(\text{R}^1)_2\text{SO}_4$; $\text{R}^1\text{OSO}_2\text{V}$; or $\text{R}^1\text{-hal}$;
optional base
(hal = F, Cl, Br, or I)
(V = $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, or $4\text{-CH}_3\text{-C}_6\text{H}_4$)

For example, compounds of Formula I can be prepared by the action of diazoalkane reagents of Formula 2 such as diazomethane (U = H) or
5 trimethylsilyldiazomethane (U = $(\text{CH}_3)_3\text{Si}$) on dicarbonyl compounds of Formula 1 (Method 1). Use of trimethylsilyldiazomethane requires a protic cosolvent such as methanol. For examples of these procedures, see *Chem. Pharm. Bull.*, (1984), 32, 3759.

As indicated in Method 2, compounds of Formula I can also be prepared by contacting carbonyl compounds of Formula 1 with alkyl trichloroacetimidates of
10 Formula 3 and a Lewis acid catalyst. Suitable Lewis acids include trimethylsilyl triflate and tetrafluoroboric acid. The alkyl trichloroacetimidates can be prepared from the appropriate alcohol and trichloroacetonitrile as described in the literature (J. Danklmaier and H. Hönig, *Synth. Commun.*, (1990), 20, 203).

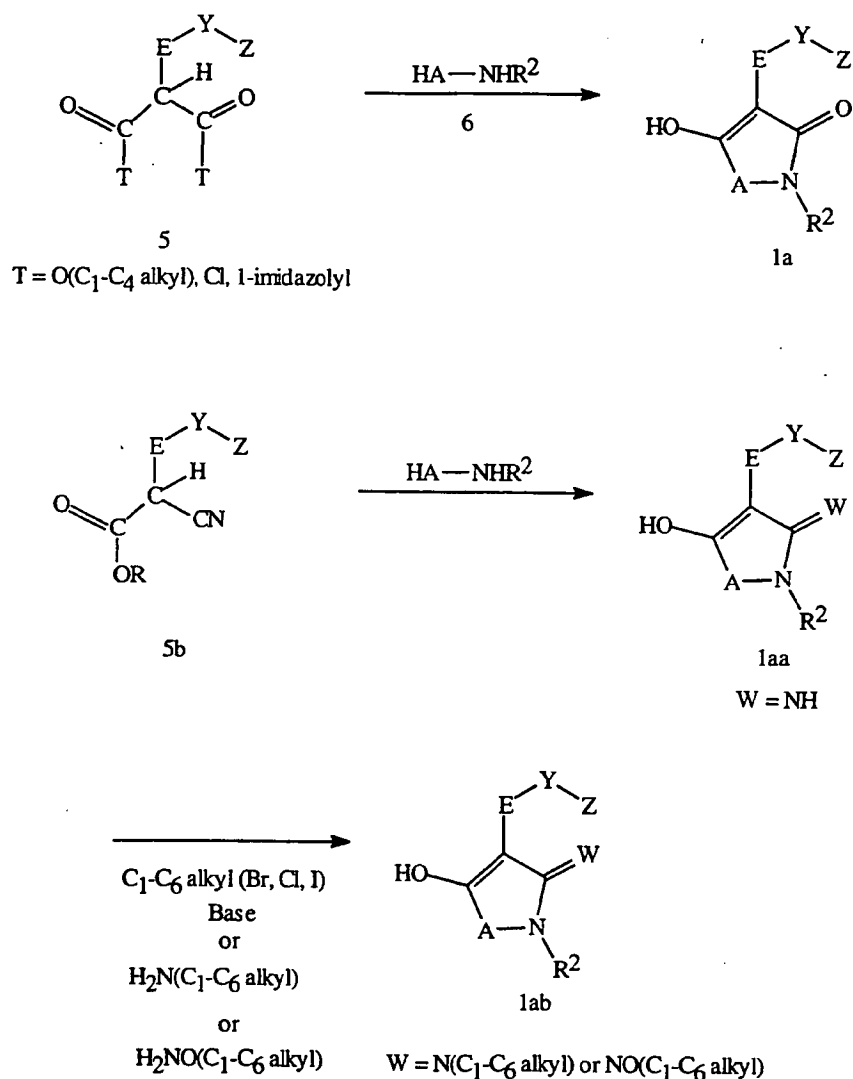
Compounds of Formula I can also be prepared from compounds of Formula 1 by
15 treatment with a trialkyloxonium tetrafluoroborate (i.e., Meerwein's salt) of Formula 4 (Method 3). The use of trialkyloxonium salts as powerful alkylating agents is well

known in the art (see U. Schöllkopf, U. Groth, C. Deng, *Angew. Chem., Int. Ed. Engl.*, (1981), 20, 798).

Other alkylating agents which can convert carbonyl compounds of Formula 1 to compounds of Formula I are dialkyl sulfates such as dimethyl sulfate, haloalkyl sulfonates
5 such as methyl trifluoromethanesulfonate, and alkyl halides such as iodomethane and propargyl bromide (Method 4). These alkylations can be conducted with or without additional base. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, or tertiary amines such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene
10 (DBU), and triethylenediamine. See R. E. Benson, T. L. Cairns, *J. Am. Chem. Soc.*, (1948), 70, 2115 for alkylation examples using agents of this type.

Compounds of Formula 1a (compounds of Formula 1 wherein G = C, W = O and X = OH) can be prepared by condensation of malonates or malonate derivatives of
15 Formula 5 with an ambident nucleophile of Formula 6 (Scheme 2). The nucleophiles of Formula 6 are *N*-substituted hydroxylamines (HO-NHR²) and substituted hydrazines (HN(R⁵)-NHR²). Examples of such nucleophiles are *N*-methylhydroxylamine and methylhydrazine. The malonate esters of Formula 5 can be prepared by methods described hereinafter. The esters of Formula 5 can also be activated by first hydrolyzing
20 the ester to form the corresponding carboxylic acid, and then converting the acid into the acid chloride (T = Cl) using thionyl chloride or oxalyl chloride, or into the acyl imidazole (T = 1-imidazolyl) by treating with 1,1'-carbonyldiimidazole. Compounds of Formula 1aa can be prepared by reaction of nitrile esters of Formula 5b with ambident
25 nucleophiles of Formula 6. See M. Scobie and G. Tennant, *J. Chem. Soc., Chem. Comm.*, (1994), 2451. Alkylation of 1aa with alkyl halides in the presence of base provides compounds of Formula 1ab. Alternatively, treatment of 1aa with alkylamines or alkoxyamines provides compounds of Formula 1ab.

Scheme 2

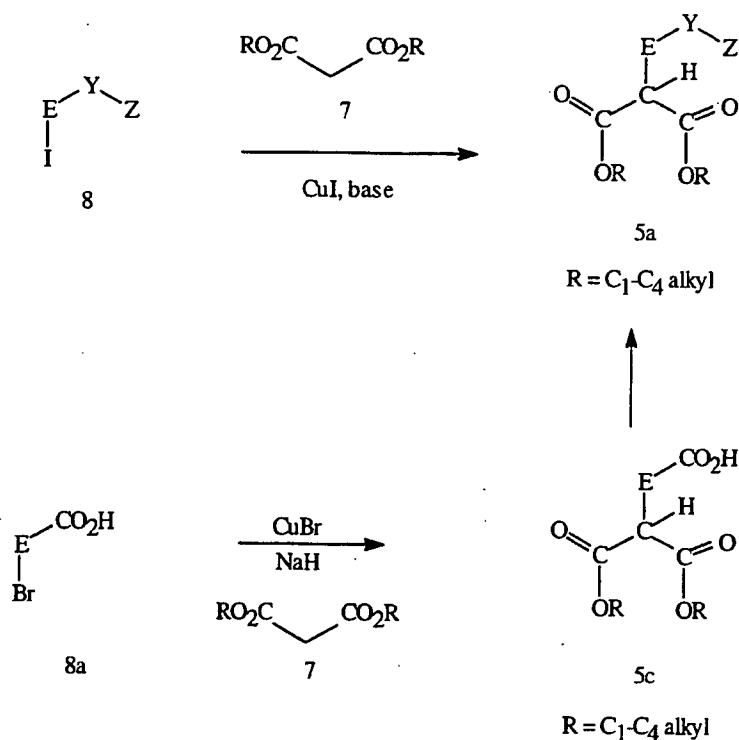


- 5 Esters of Formula 5a can be prepared from copper (I)-catalyzed reaction of malonate esters of Formula 7 with substituted aryl halides of Formula 8 according to methods adapted from A. Osuka, T. Kobayashi and H. Suzuki, *Synthesis*, (1983), 67 and M. S. Malamas, T. C. Hohman, and J. Millen, *J. Med. Chem.*, 1994, 37, 2043-2058, and illustrated in Scheme 3. Procedures to prepare compounds of Formula 8 are described
- 10 below (see Scheme 32).

Malonate esters of Formula 5a can also be prepared from diester carboxylic acids of Formula 5c after modification of the carboxylic acid functional group to the appropriate Y and Z group. A copper (I)-catalyzed coupling of malonates of Formula 7

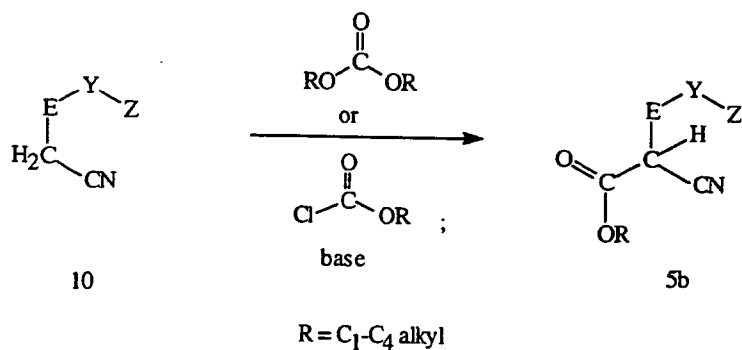
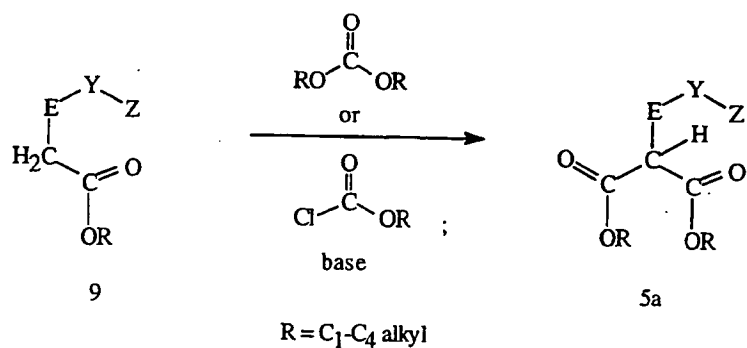
with orthobromocarboxylic acids of Formula 8a (see A. Bruggink, A. McKillop, *Tetrahedron*, (1975), 31, 2607) can be used to prepare compounds of Formula 5c as shown in Scheme 3. Methods to prepare compounds of Formula 8a are common in the art (see P. Beak, V. Snieckus, *Acc. Chem. Res.*, (1982), 15, 306 and *Org. React.*, (1979), 26, 1 and references therein).

Scheme 3



Additionally, the malonate esters of Formula 5a can be prepared by treating aryl acetic acid esters of Formula 9 with a dialkyl carbonate or alkyl chloroformate in the presence of a suitable base such as, but not limited to, sodium metal or sodium hydride (Scheme 4). For example, see *J. Am. Chem. Soc.*, (1928), 50, 2758. Nitrile esters of Formula 5b can be prepared similarly from compounds of Formula 10.

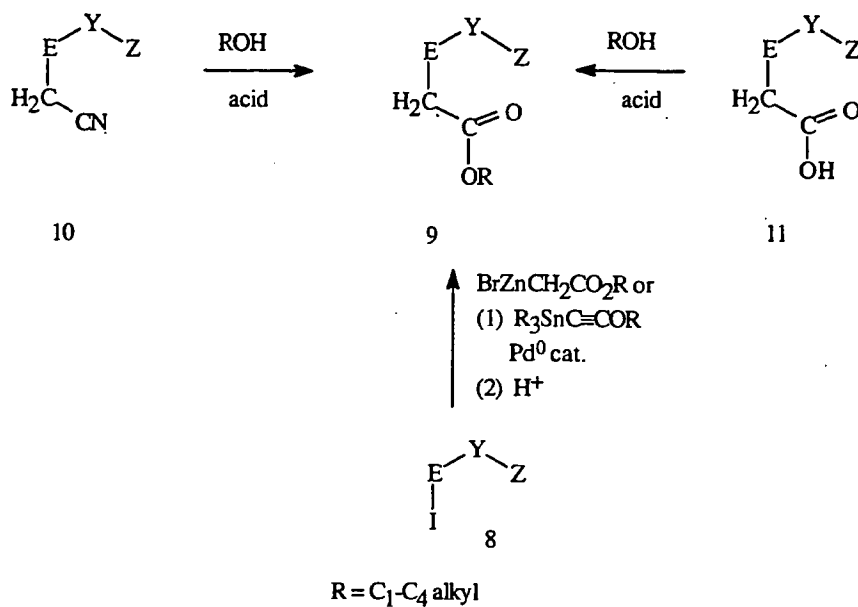
21

Scheme 4

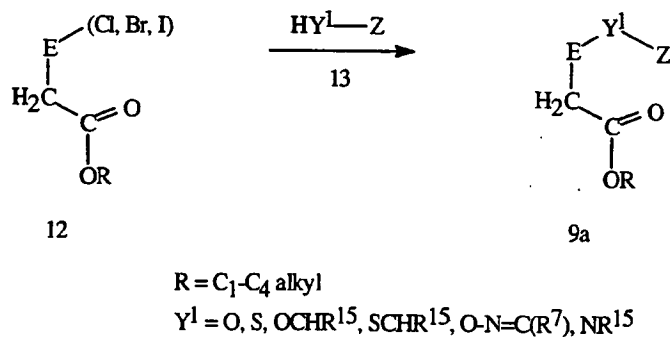
5 Esters of Formula 9 can be prepared from acid-catalyzed alcoholysis of aryl acetonitriles of Formula 10 or esterification of aryl acetic acids of Formula 11 as illustrated in Scheme 5 (see *Org. Synth.*, Coll. Vol. I, (1941), 270).

10 Additionally, esters of formula 9 can be prepared by palladium (0)-catalyzed cross coupling reaction of aryl iodides of Formula 8 with a Reformatsky reagent or an alkoxy(trialkylstannyl)acetylene followed by hydration (Scheme 5). For example, see T. Sakamoto, A. Yasuhara, Y. Kondo, H. Yamanaka, *Synlett.*, (1992), 502, and J. F. Fauvarque, A. Jutard, *J. Organometal. Chem.*, (1977), 132, C17.

22

Scheme 5

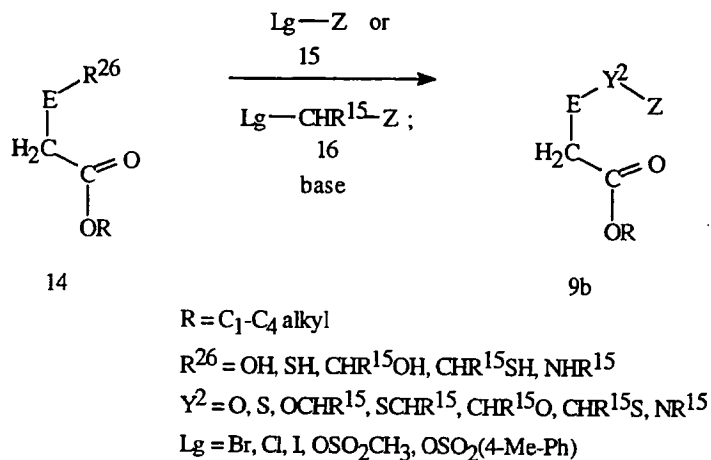
Aryl acetic acid esters of Formula 9a can also be prepared by copper (I)-catalyzed condensation of aryl halides of Formula 12 with compounds of Formula 13 as described in EP-A-307,103 and illustrated below in Scheme 6.

Scheme 6

Some esters of Formula 9 (Formula 9b) can also be prepared by forming the Y² bridge using conventional nucleophilic substitution chemistry (Scheme 7). Displacement of an appropriate leaving group (Lg) in electrophiles of Formula 15 or 16 with a nucleophilic ester of Formula 14 affords compounds of Formula 9b. A base, for example

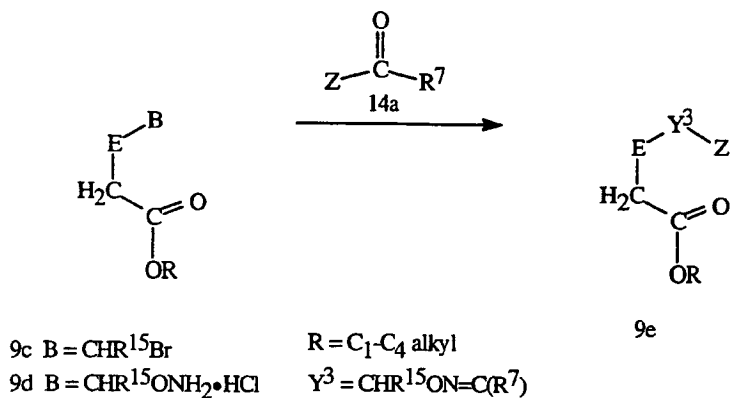
sodium hydride, is used to generate the corresponding alkoxide or thioalkoxide of the compound of Formula 14.

Scheme 7



- 5 Some esters of Formula 9 (Formula 9e) can also be prepared by forming the Y^3 bridge from substituted hydroxylamine 9d and carbonyl compounds 14a. The hydroxylamine 9d is in turn prepared from esters 9c. This method has been described in EP-A-600,835 and illustrated in Scheme 8.

Scheme 8



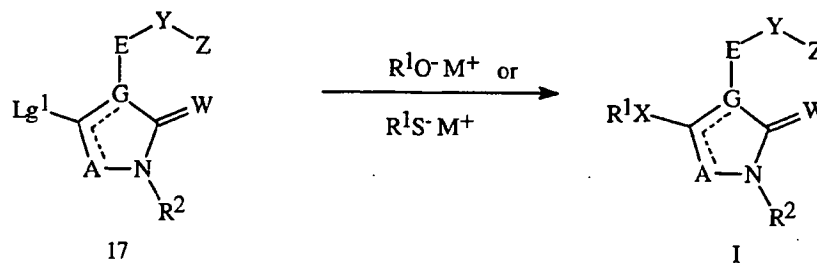
10

2) Displacement and Conjugate Addition/Elimination Procedures

Compounds of Formula I can also be prepared by reaction of Formula 17 compounds with alkali metal alkoxides ($\text{R}^1\text{O}^-\text{M}^+$) or alkali metal thioalkoxides ($\text{R}^1\text{S}^-\text{M}^+$)

in a suitable solvent (Scheme 9). The leaving group Lg^1 in the amides of Formula 17 are any group known in the art to undergo a displacement reaction of this type. Examples of suitable leaving groups include chlorine, bromine, and sulfonyl and sulfonate groups. Examples of suitable inert solvents are dimethylformamide or dimethyl sulfoxide.

5

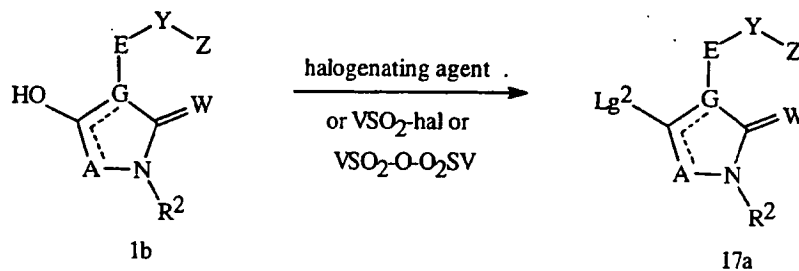
Scheme 9

$\text{Lg}^1 = \text{Cl}, \text{Br}, -\text{SO}_2\text{V}, \text{ or } -\text{OSO}_2\text{V}$

$\text{V} = \text{C}_1\text{-C}_6 \text{ alkyl}, \text{C}_1\text{-C}_6 \text{ haloalkyl}, \text{ or } 4\text{-CH}_3\text{-C}_6\text{H}_4$

$\text{M} = \text{K or Na}$

Compounds of Formula 17a can be prepared from compounds of Formula 1b (compounds of Formula 1 wherein X is OH) by reaction with halogenating agents such as thionyl chloride or phosphorus oxybromide to form the corresponding β -halo-substituted derivatives (Scheme 10). Alternatively, compounds of Formula 1b can be treated with an alkylsulfonyl halide or haloalkylsulfonyl anhydride, such as methanesulfonyl chloride, *p*-toluenesulfonyl chloride, and trifluoromethanesulfonyl anhydride, to form the corresponding β -alkylsulfonate of Formula 17a. The reaction with the sulfonyl halides may be performed in the presence of a suitable base (e.g., triethylamine).

Scheme 10

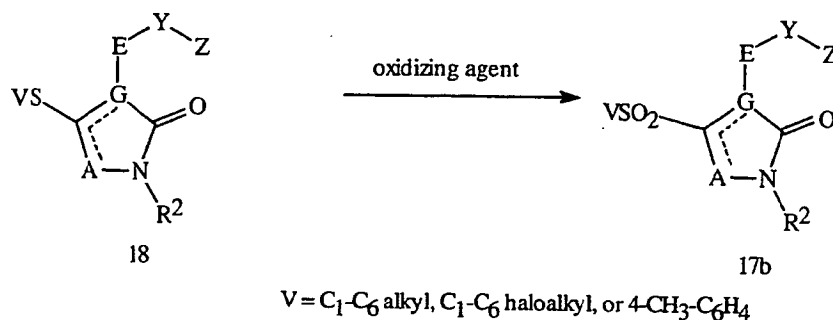
$\text{Lg}^2 = \text{Cl}, \text{Br}, \text{ or } -\text{OSO}_2\text{V}$

$\text{V} = \text{C}_1\text{-C}_6 \text{ alkyl}, \text{C}_1\text{-C}_6 \text{ haloalkyl}, \text{ or } 4\text{-CH}_3\text{-C}_6\text{H}_4$

$\text{hal} = \text{Br}, \text{Cl or F}$

As illustrated in Scheme 11, sulfonyl compounds of Formula 17b can be prepared by oxidation of the corresponding thio compound of Formula 18 using well-known methods for the oxidation of sulfur (see Schrenk, K. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S. et al., Eds.; Wiley: New York, 1988). Suitable oxidizing reagents include meta-chloro-peroxybenzoic acid, hydrogen peroxide and Oxone® (KHSO₅).

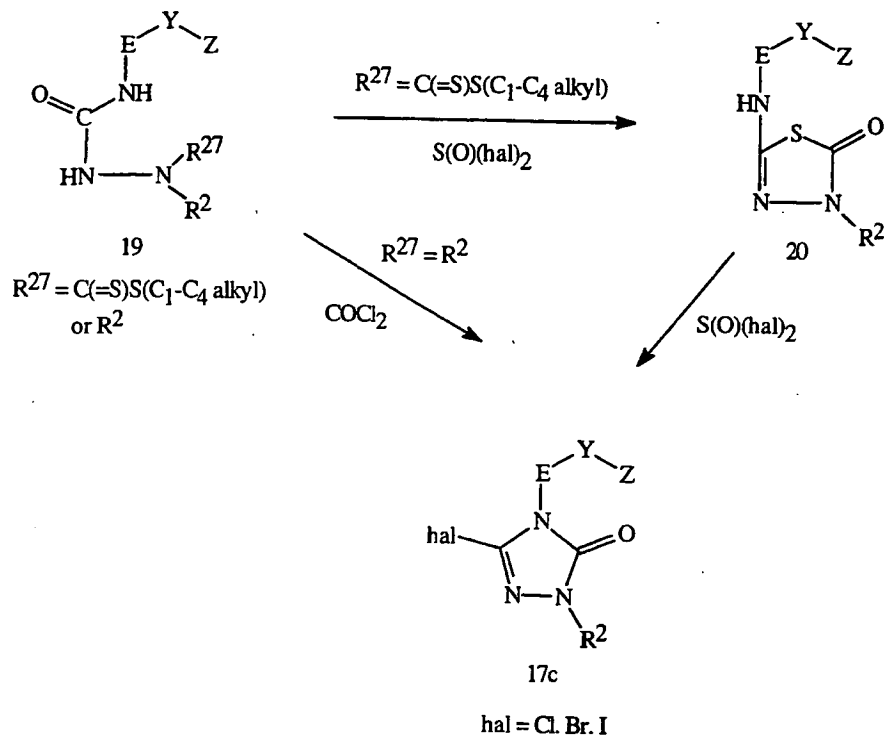
Scheme 11



Alternatively, halo-compounds of Formula 17c (compounds of Formula 17a wherein A = N, G = N, and W = O) can be prepared from hydrazides of Formula 19 as illustrated in Scheme 12. When R²⁷ = C(=S)S(C₁-C₄ alkyl), the diacyl compound of Formula 19 is treated with excess thionyl halide, for example excess thionyl chloride. The product formed first is the ring-closed compound of Formula 20 which can be isolated or converted *in situ* to the compound of Formula 17c; see P. Molina, A. Tárraga, A. Espinosa, *Synthesis*, (1989), 923 for a description of this process.

Alternatively, when R²⁷ = R² as defined above, the hydrazide of Formula 19 is cyclized with phosgene to form the cyclic urea of Formula 17c wherein hal = Cl. This procedure is described in detail in *J. Org. Chem.*, (1989), 54, 1048.

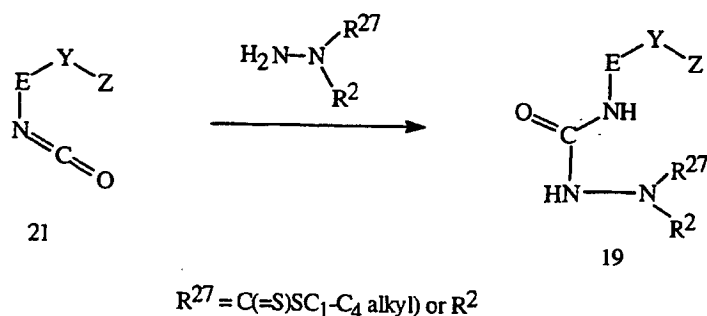
26

Scheme 12

The hydrazides of Formula 19 can be prepared as illustrated in Scheme 13.

Condensation of the isocyanate of Formula 21 with the hydrazine of

- 5 Formula $\text{H}_2\text{NNR}^2\text{R}^{27}$ in an inert solvent such as tetrahydrofuran affords the hydrazide.

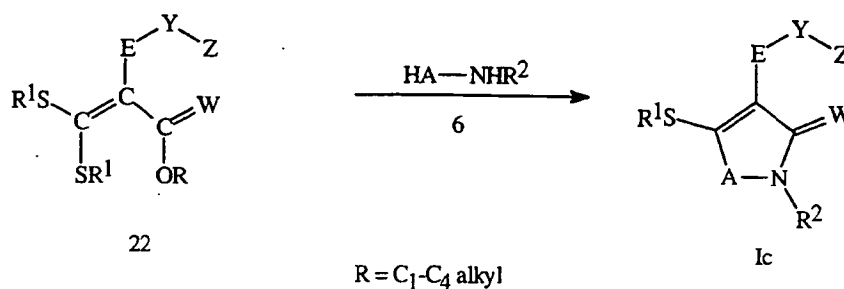
Scheme 13

3) Conjugate Addition/Cyclization Procedures

- 10 In addition to the methods disclosed above, compounds of Formula I wherein $X = \text{SR}^1$ and $G = \text{C}$ (Formula Ic) can be prepared by treating a ketenedithioacetal of

Formula 22 with an ambident nucleophile of Formula 6 (Scheme 14). The nucleophiles of Formula 6 are described above.

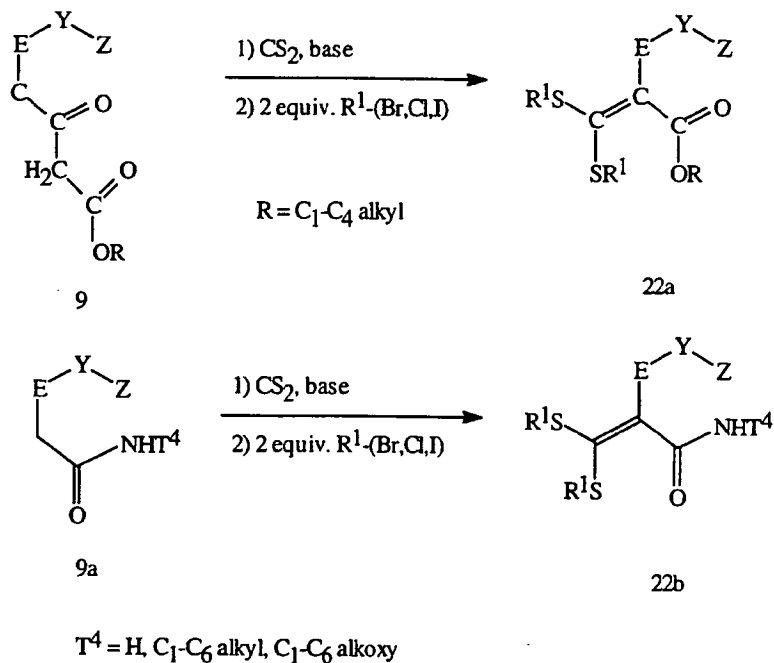
Scheme 14



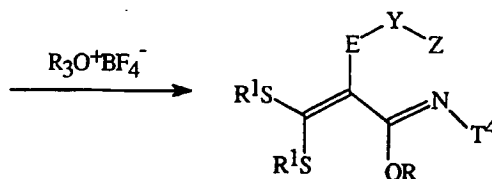
- 5 Ketene dithioacetals of Formula 22a or 22b can be prepared by condensing aryl acetic esters of Formula 9 or amides of Formula 9a, respectively, with carbon disulfide in the presence of a suitable base, followed by reaction with two equivalents of an R^1 -halide, such as iodomethane or propargyl bromide (Scheme 15). Conversion of 22b to 22c can be accomplished by reaction with trialkyl tetrafluoroborates.

10

Scheme 15



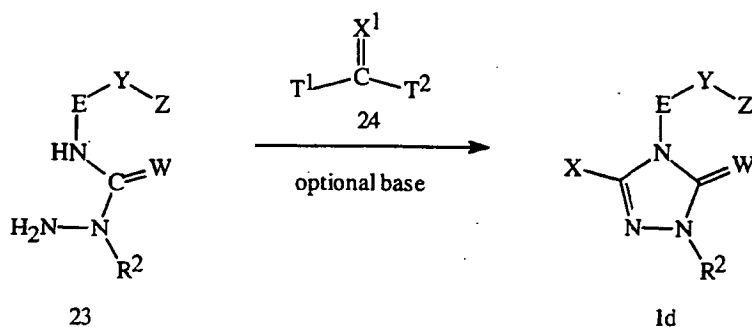
28



Compounds of Formula 1d (compounds of Formula 1 wherein A = N, G = N) can be prepared by condensation of *N*-amino-ureas of Formula 23 with a carbonylating agent of Formula 24 (Scheme 16). The carbonylating agents of Formula 24 are carbonyl or thiocarbonyl transfer reagents such as phosgene, thiophosgene, diphosgene (ClC(=O)OCCl₃), triphosgene (Cl₃COC(=O)OCCl₃), *N,N'*-carbonyldiimidazole, *N,N'*-thiocarbonyldiimidazole, and 1,1'-carbonyldi(1,2,4-triazole). Alternatively, the compounds of Formula 24 can be alkyl chloroformates or dialkyl carbonates. Some of these carbonylating reactions may require the addition of a base to effect reaction. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, tertiary amines such as triethylamine and triethylenediamine, pyridine, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Suitable solvents include polar aprotic solvents such as acetonitrile, dimethylformamide, or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; or halocarbons such as dichloromethane or chloroform. The reaction temperature can vary between 0°C and 150°C and the reaction time can be from 1 to 72 hours depending on the choice of base, solvent, temperature, and substrates.

20

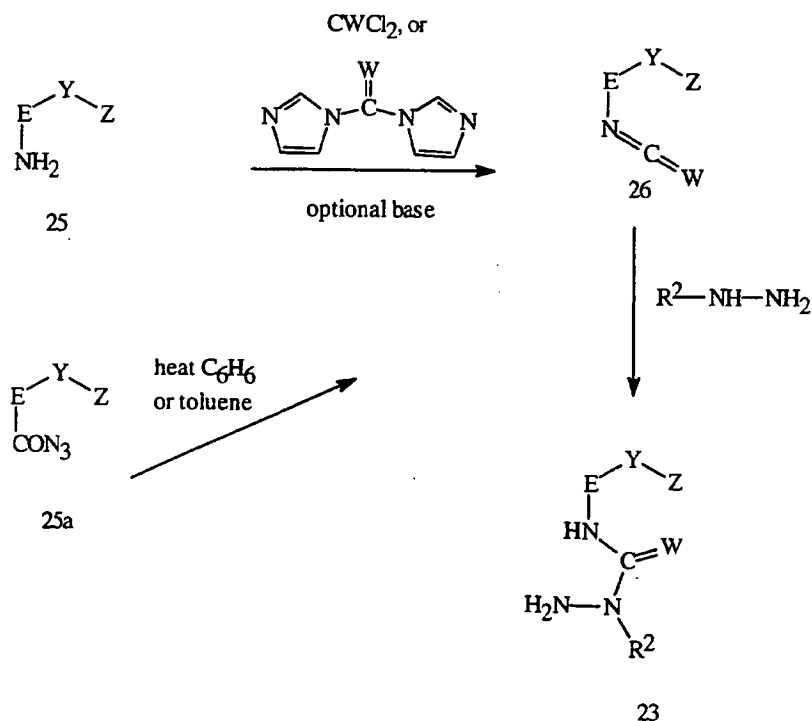
Scheme 16



T¹ and T² are independently Cl, OCCl₃, O(C₁-C₄ alkyl), 1-imidazolyl, 1,2,4-triazolyl
 X = OH or SH
 X¹ = O or S

- N*-Amino-ureas of Formula 23 can be prepared as illustrated in Scheme 17.
- Treatment of an arylamine of Formula 25 with phosgene, thiophosgene, *N,N'*-carbonyldiimidazole, or *N,N'*-thiocarbonyldiimidazole produces the isocyanate or isothiocyanate of Formula 26. A base can be added for reactions with phosgene or thiophosgene.
- 5 Isocyanates of Formula 26 can also be prepared by heating acylazides of Formula 25a in a solvent such as toluene or benzene (Curtius rearrangement). The corresponding acylazides can be prepared from well known methods in the art (see March, J., *Advanced Organic Chemistry*; 3rd Edition, John Wiley: New York, (1985), pp 428, 637 and also *Chem. Pharm. Bull* (1977), 25, 165, and references therein.
- 10 Subsequent treatment of the iso(thio)cyanate with an R^2 -substituted hydrazine produces the *N*-amino-urea of Formula 23.

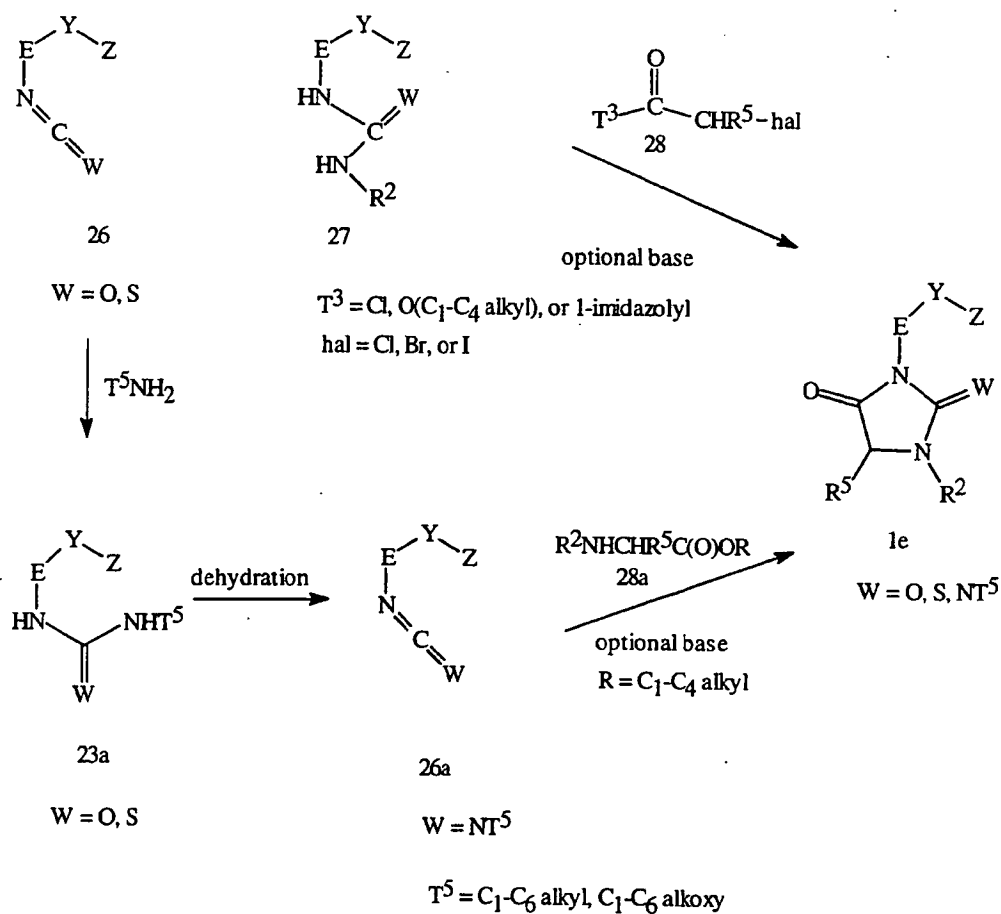
Scheme 17



- 15 Compounds of Formula 1e (compounds of Formula 1 wherein $A = CR^5$, $G = N$, and $X = O$) can be prepared by either method illustrated in Scheme 18. Ureas of Formula 27 are reacted with activated 2-halocarboxylic acid derivatives such as 2-halocarboxylic acid chlorides, 2-halocarboxylic acid esters or 2-haloacyl imidazoles. The initial acylation on the arylamino nitrogen is followed by an intramolecular

- displacement of the 2-halo group to effect cyclization. Base may be added to accelerate the acylation and/or the subsequent cyclization. Suitable bases include triethylamine and sodium hydride. Alternatively, Formula 1e compounds can be prepared by reaction of Formula 26 iso(thio)cyanates or Formula 26a carbodiimides with Formula 28a esters. As described above, base may be added to accelerate the reaction and subsequent cyclization to Formula 1e compounds. Carbodiimides 26a can be prepared as shown in Scheme 18, starting with compounds of Formula 26.

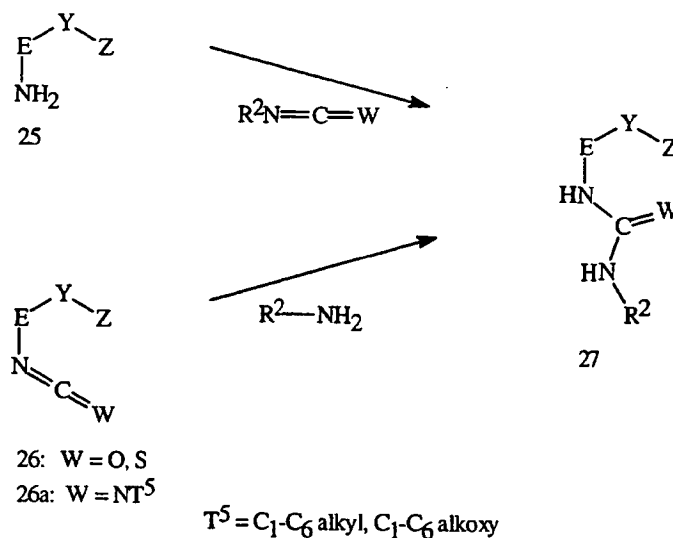
Scheme 18



The (thio)ureas or amidines of Formula 27 can be prepared by either of the methods illustrated in Scheme 19. The arylamine of Formula 25 can be contacted with an isocyanate or isothiocyanate of Formula $\text{R}^2\text{N}=\text{C}=\text{W}$ as described above. Alternatively, an iso(thio)cyanate of Formula 26 or carbodiimide of Formula 26a can be

- condensed with an amine of Formula R^2-NH_2 to form the urea or amidine. The arylamine and iso(thio)cyanates of Formulae 25 and 26, respectively, are commercially available or prepared by well-known methods. For example, isothiocyanates can be prepared by methods described in *J. Heterocycl. Chem.*, (1990), 27, 407. Isocyanates can be prepared as described in March, J., *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), pp 944, 1166 and also in *Synthetic Communications*, (1993), 23 (3), 335 and references therein. For methods describing the preparation of arylamines of Formula 25 that are not commercially available, see M. S. Gibson, *In The Chemistry of the Amino Group*; Patai, S., Ed.; Interscience Publishers, 1968; p 37 and *Tetrahedron Lett.* (1982), 23 (7), 699 and references therein.

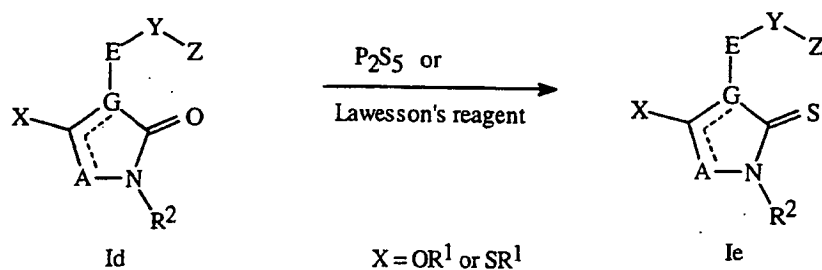
Scheme 19



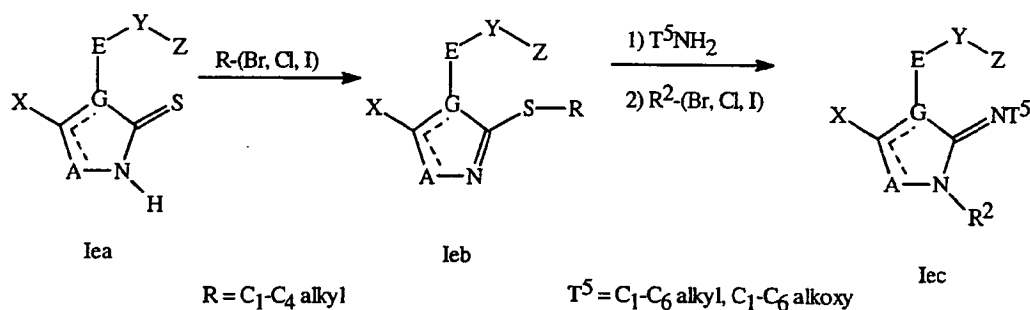
4) Thionation Procedures

- Compounds of Formula Ie, compounds of Formula I wherein $W = S$, can be prepared by treating compounds of Formula Id (I wherein $W = O$) with thionating reagents such as P_2S_5 or Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide) as illustrated in Scheme 20 (see *Bull. Soc. Chim. Belg.*, (1978), 87, 229; and *Tetrahedron Lett.*, (1983), 24, 3815).

32

Scheme 20

Reaction of compounds of Formula Iea with an alkyl halide in the presence of base provides compounds of Formula Ieb, which can be reacted with compounds of Formula T^5NH_2 and then alkylated with $\text{R}^2\text{-(Br, Cl, or I)}$ to provide compounds of Formula Iec.

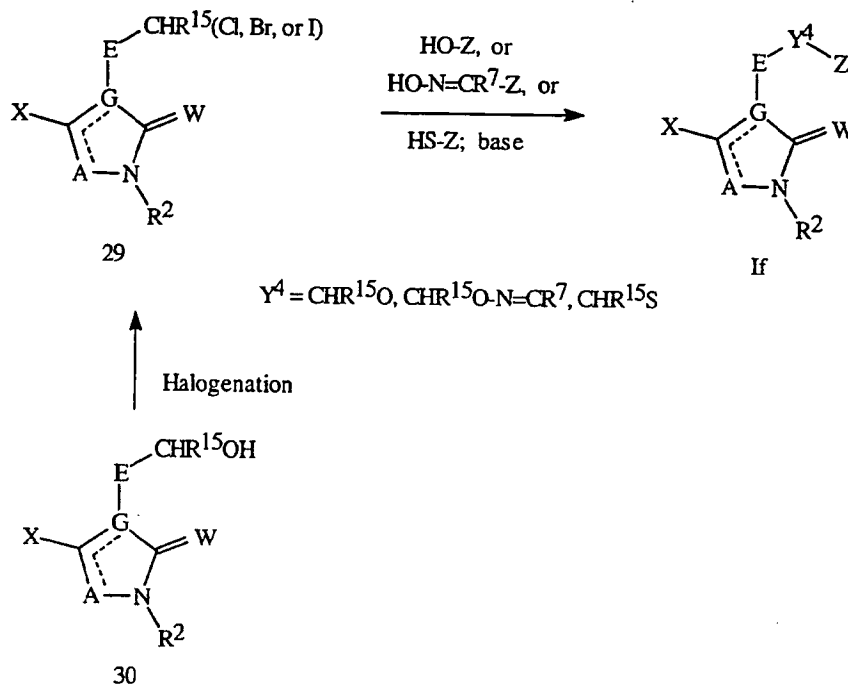
Scheme 20a5) Aryl Moiety (E-Y-Z) Synthesis Procedures

- 10 Compounds of Formula If (compounds of Formula I wherein Y is CHR^{15}O , CHR^{15}S , or $\text{CHR}^{15}\text{O-N=CR}^7$) can be prepared by contacting halides of Formula 29 with various nucleophiles (Scheme 21). The appropriate alcohol or thiol is treated with a base, for example sodium hydride, to form the corresponding alkoxide or thioalkoxide which acts as the nucleophile.

15

33

Scheme 21

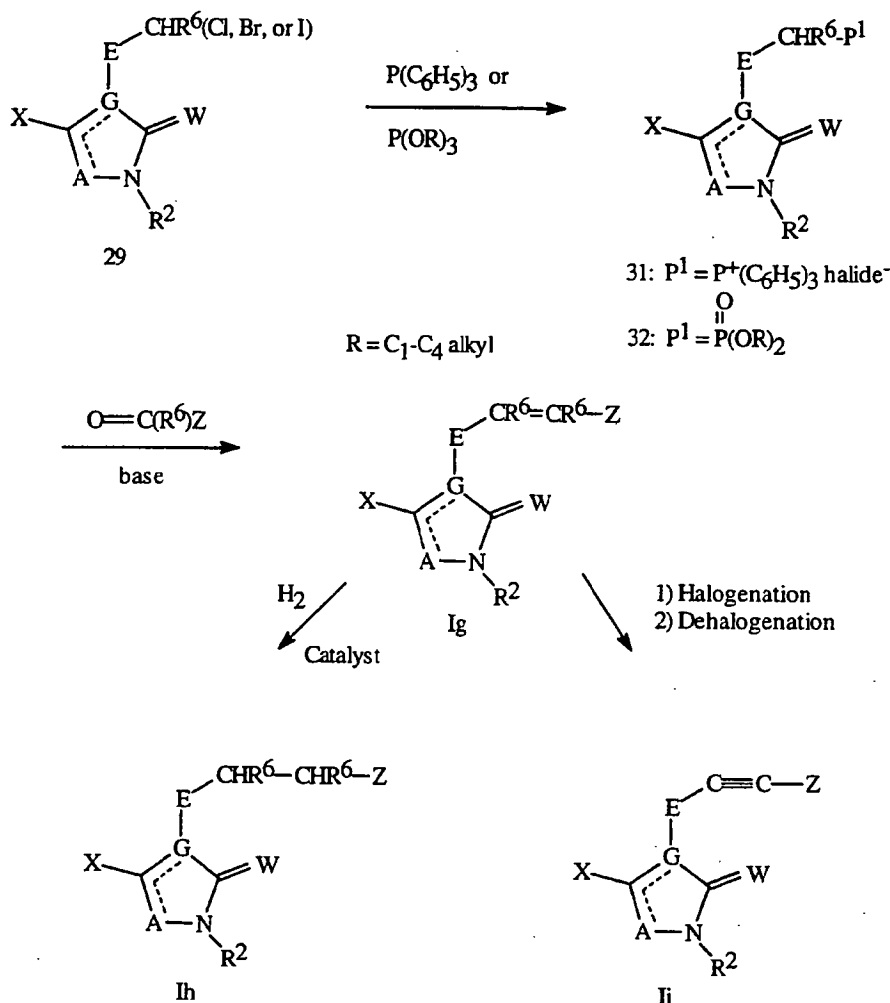


Some aryl halides of Formula 29 can be prepared by radical halogenation of the corresponding alkyl compound (i.e., H instead of halogen in Formula 29), or by acidic cleavage of the corresponding methyl ether (i.e., OMe instead of halogen in Formula 29). Other aryl halides of Formula 29 can be prepared from the appropriate alcohols of Formula 30 by well known halogenation methods in the art (see Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; 3rd ed., Part B, Plenum: New York, (1990), p 122).

Compounds of Formula I wherein Y is $\text{CR}^6=\text{CR}^6$ or $\text{CHR}^6\text{-CHR}^6$ (Formula Ig and Ih, respectively) can be prepared as illustrated in Scheme 22. Treatment of the halides of Formula 29 with triphenylphosphine or a trialkylphosphite produces the corresponding phosphonium salt (Formula 31) or phosphonate (Formula 32), respectively. Condensation of the phosphorus compound with a base and a carbonyl compound of Formula $\text{Z(R}^6\text{)C=O}$ affords the olefin of Formula Ig.

34

Scheme 22



- The olefins of Formula Ig can be converted to the saturated compounds of
- 5 Formula Ih by hydrogenation over a metal catalyst such as palladium on carbon as is well-known in the art (Rylander, *Catalytic Hydrogenation in Organic Synthesis*; Academic: New York, 1979).

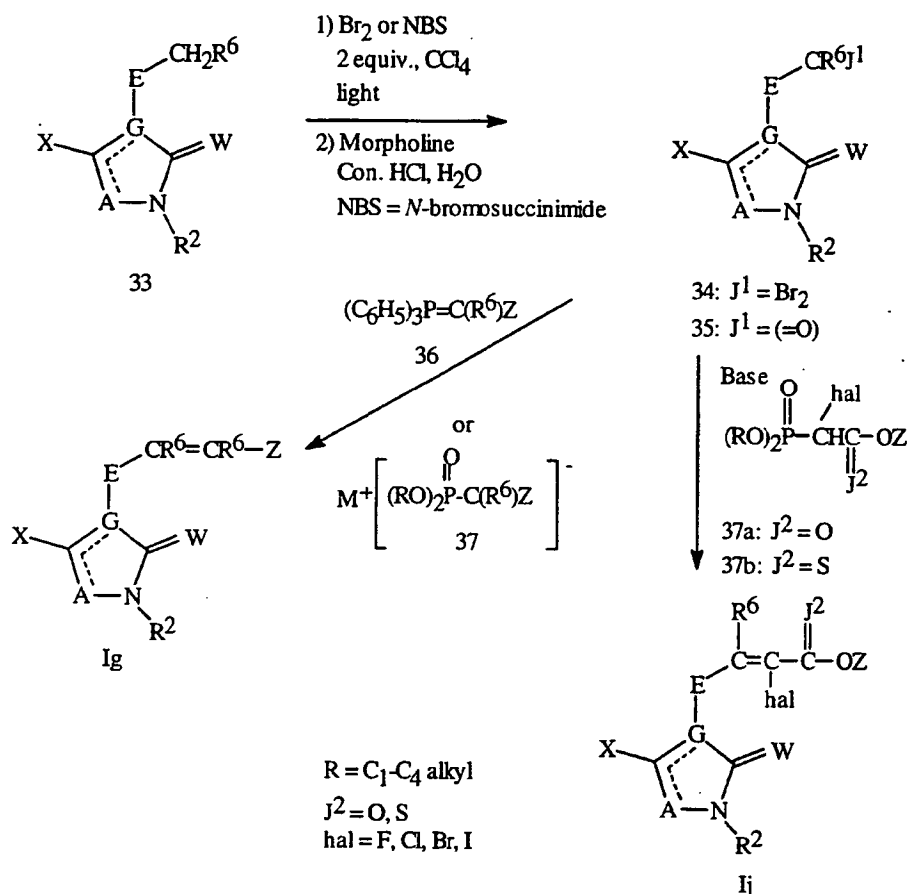
- Formula Ii alkynes can be prepared by halogenation/dehalogenation of Formula Ig olefins using procedures well-known in the art (March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), p 924). Additionally, Formula Ii alkynes can be
- 10 prepared by well-known reaction of aryl halides with alkyne derivatives in the presence of catalysts such as nickel or palladium (see *J. Organomet. Chem.*, (1975), 93 253-257).

The olefin of Formula Ig can also be prepared by reversing the reactivity of the reactants in the Wittig or Horner-Emmons condensation. For example, 2-alkylaryl

- derivatives of Formula 33 can be converted into the corresponding dibromo-compound of Formula 34 as illustrated in Scheme 23 (see *Synthesis*, (1988), 330). The dibromo-compound can be hydrolyzed to the carbonyl compound of Formula 35, which in turn can be condensed with a phosphorus-containing nucleophile of Formula 36 or 37 to
- 5 afford the olefin of Formula Ig. Carbonyl compounds of Formula 35 can also be prepared by oxidation of halides of Formula 29 in Scheme 22 (see *Tetrahedron Lett.*, (1990), 31, 4825 and *Bull. Chem. Soc. Jpn.*, (1981), 54, 2221 and references therein). Additionally, compounds of Formula 35 can be prepared by oxidation of the corresponding alcohols of Formula 30.
- 10 Vinylhalides of Formula Ij can be prepared by reacting phosphorus reagents of Formulae 37a or 37b with carbonyl compounds of Formula 35 (Scheme 23). The preparations of halides of Formula 37a from the appropriate diethylphosphonoacetate are described by McKenna and Khawli in *J. Org. Chem.*, (1986), 51, 5467. The thiono esters of Formula 37b can be prepared from esters of Formula 37a by converting the
- 15 carbonyl oxygen of the ester to a thiocarbonyl (see *Chem. Rev.*, (1984), 84, 17 and *Tetrahedron Lett.*, (1984), 25, 2639).

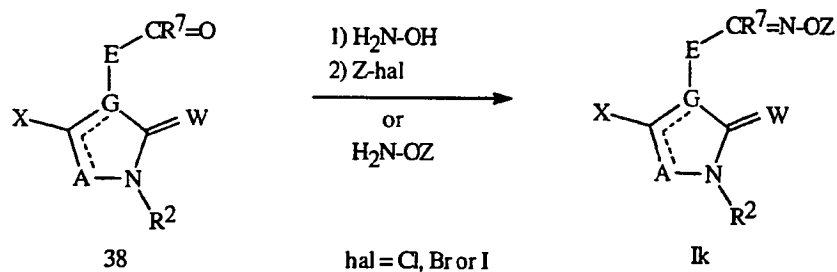
36

Scheme 23



- Oximes of Formula Ik (Formula I wherein Y is $\text{C}(\text{R}^7)=\text{N}-\text{O}$) can be prepared from carbonyl compounds of Formula 38 by condensation with hydroxylamine, followed by *O*-alkylation with electrophiles of Formula Z-(Cl, Br, or I) (Scheme 24). Alternatively, the *O*-substituted hydroxylamine can be condensed with the carbonyl compound of Formula 38 to yield oximes of Formula Ik directly.

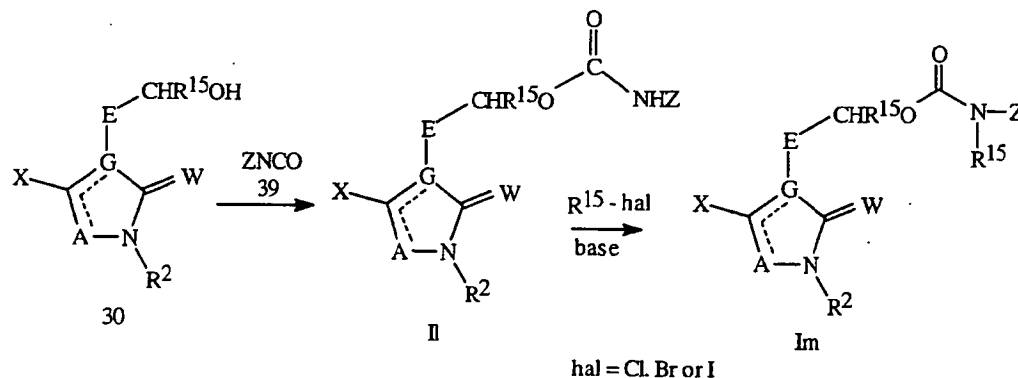
Scheme 24



Carbamates of Formula II can be prepared by reacting aryl alcohols of Formula 30 with isocyanates of Formula 39 (Scheme 25). A base such as triethylamine can be added to catalyze the reaction. As shown, carbamates of Formula II can be further alkylated to provide the carbamates of Formula Im.

5

Scheme 25



Compounds of Formula I wherein Y is $-\text{CHR}^{15}\text{O}-\text{N}=\text{C}(\text{R}^7)-\text{C}(=\text{N}-\text{A}^2-\text{Z}^1)-\text{A}^1-$, $-\text{CHR}^{15}\text{O}-\text{N}=\text{C}(\text{R}^7)-\text{C}(\text{R}^7)=\text{N}-\text{A}^2-\text{A}^3-$ or $-\text{CHR}^{15}\text{O}-\text{N}=\text{C}(-\text{C}(\text{R}^7)=\text{N}-\text{A}^2-\text{Z}^1)-$ can be prepared by methods known in the art or obvious modifications (see, for example, WO 95/18789, WO 95/21153, and references therein) together with the methods disclosed herein.

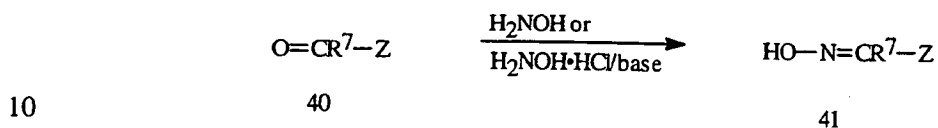
Compounds of Formula I wherein Y is $-\text{CHR}^{15}\text{OC}(=\text{O})\text{O}-$, $-\text{CHR}^{15}\text{OC}(=\text{S})\text{O}-$, $-\text{CHR}^{15}\text{OC}(=\text{O})\text{S}-$, $-\text{CHR}^{15}\text{OC}(=\text{S})\text{S}-$, $-\text{CHR}^{15}\text{SC}(=\text{O})\text{N}(\text{R}^{15})-$, $-\text{CHR}^{15}\text{SC}(=\text{S})\text{N}(\text{R}^{15})-$, $-\text{CHR}^{15}\text{SC}(=\text{O})\text{O}-$, $-\text{CHR}^{15}\text{SC}(=\text{S})\text{O}-$, $-\text{CHR}^{15}\text{SC}(=\text{O})\text{S}-$, $-\text{CHR}^{15}\text{SC}(=\text{S})\text{S}-$, $-\text{CHR}^{15}\text{SC}(=\text{NR}^{15})\text{S}-$ or $-\text{CHR}^{15}\text{N}(\text{R}^{15})\text{C}(=\text{O})\text{N}(\text{R}^{15})-$ can be prepared by methods known in the art or obvious modifications (see, for example, U.S. 5416110-A, EP 656351-A1 and references therein) together with the methods disclosed herein.

The compounds of the present invention are prepared by combinations of reactions as illustrated in the Schemes 1-25 in which Z is a moiety as described in the summary. Preparation of the compounds containing the radical Z as described in the summary, substituted with L (defined as any group attached to Z as depicted in each of the individual schemes) can be accomplished by one skilled in the art by the appropriate combination of reagents and reaction sequences for a particular Z-L. Such reaction sequences can be developed based on known reactions available in the chemical art. For a general reference, see March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley:

New York, (1985) and references therein. See the following paragraphs for some examples of how L is defined in individual schemes, and the preparation of representative Z-L examples.

Compounds of Formula 41 in Scheme 26 can be prepared from compounds of Formula 40 by reaction with hydroxylamine or hydroxylamine salts. See Sandler and Karo, "Organic Functional Group Preparations," Vol. 3 Academic Press, New York, (1972) 372-381 for a review of methods. Compounds of Formula 41 correspond to compounds of Formula 13 in Scheme 6 when $Y^1 = O-N=C(R^7)$ and in Scheme 21, reagent $HO-N=CR^7$.

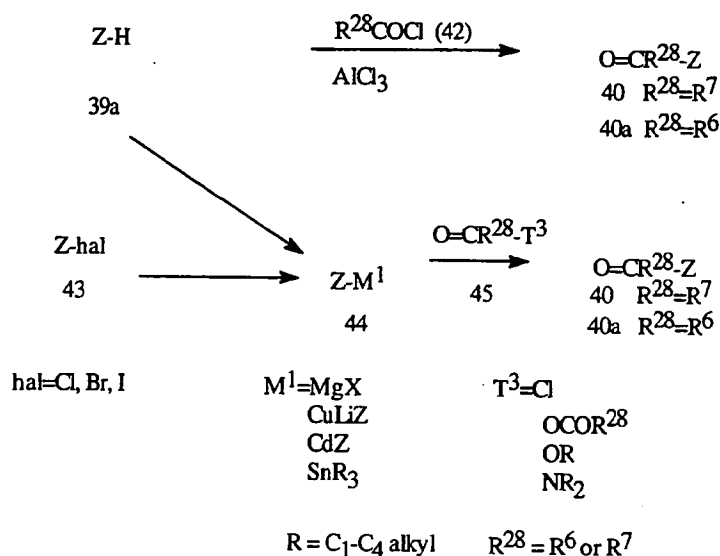
Scheme 26



Compounds of Formula 40 can be prepared from compounds of Formula 39a (Scheme 27) by Friedel-Crafts acylation with compounds of Formula 42. (See Olah, G. "Friedel-Crafts and Related Reactions," Interscience, New York (1963-1964) for a general review). Compounds of Formula 40 may also be prepared by reaction of acyl halides, anhydrides, esters, or amides of Formula 45 with organometallic reagents of Formula 44. (See March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), pp 433-435 and references therein.) The organometallic compounds of Formula 44 may be prepared by reductive metallation or halogen-metal exchange of a halogen-containing compound of Formula 43 using, for example, magnesium or an organolithium reagent, or by deprotonation of compounds of Formula 39a using a strong base such as a lithioamide or an organolithium reagent, followed by transmetallation. Compound 40 corresponds to Compound 14a in Scheme 8, while compound 40a corresponds to $O=C(R^6)Z$ in Scheme 22.

39

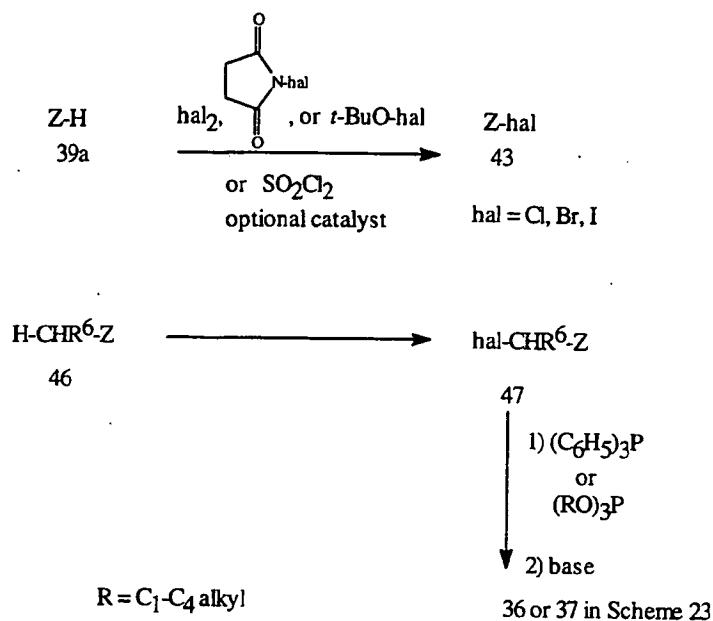
Scheme 27



- Compounds of Formula 43 may be prepared by reaction of compounds of Formula 39a (Scheme 28) with, for example, bromine or chlorine, with or without additional catalysts, under free-radical or aromatic electrophilic halogenation conditions, depending on the nature of Z. Alternative sources of halogen, such as *N*-halosuccinimides, *tert*-butyl hypohalites or SO₂Cl₂, may also be used. (See March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), pp 476-479, 620-626, and references therein.) For a review of free-radical halogenation, see Huyser, in Patai, "The Chemistry of the Carbon-Halogen Bond," Part 1, Wiley, New York (1973) pp 549-607. For electrophilic substitutions, see de la Mare, "Electrophilic Halogenation," Cambridge University Press, London (1976). Compounds of Formula 43 correspond to compounds of Formula 15 in Scheme 7 where Lg = Br, Cl, or I and reagent Z-hal in Scheme 24. Compounds of Formula 47 can be prepared from compounds of Formula 46 by similar procedures. Compounds of Formula 47 correspond to compounds of Formula 16 in Scheme 7 where Lg = Br, Cl, or I. Compounds of Formula 36 or 37 in Scheme 23 can be prepared by reaction of compounds of Formula 47 with triphenylphosphine or trialkyl phosphites, respectively, followed by deprotonation with base. See Cadogan, "Organophosphorus Reagents in Organic Synthesis," Academic Press, New York (1979) for a general treatise on these reagents.

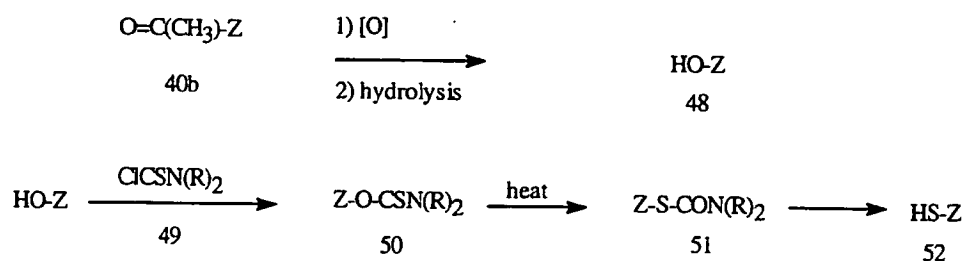
40

Scheme 28

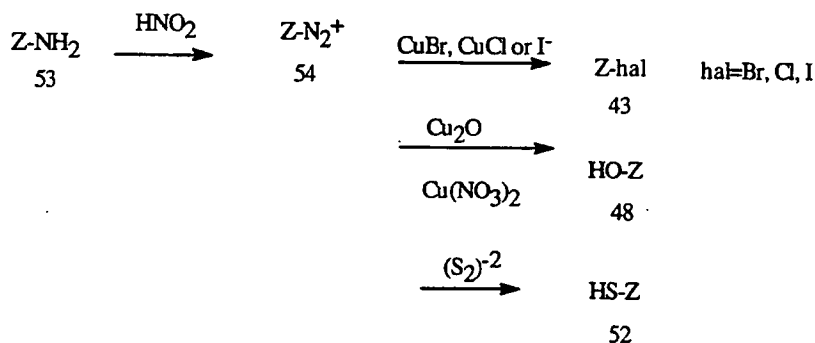


- Compounds of Formula 48 can be prepared from compounds of Formula 40b by treatment with peracids such as perbenzoic or peracetic acid, or with other peroxy compounds in the presence of an acid catalysts, followed by hydrolysis of the resultant ester. For a review, see Plesnicar, in Trahanovsky, "Oxidation in Organic Chemistry, pt. C, Academic Press, New York (1978) pp 254-267. Formula 48 corresponds to Formula 13 in Scheme 6 when $\text{Y}^1 = \text{O}$ and reagent HO-Z in Scheme 21. Compounds of Formula 52 can be prepared from compounds of Formula 48 by conversion to the dialkylthiocarbamates of Formula 50 followed by rearrangement to Formula 51 and subsequent hydrolysis. See M. S. Newman and H. A. Karnes, *J. Org. Chem.* (1966), 31, 3980-4. Formula 52 corresponds to Formula 13 in Scheme 6 when $\text{Y}^1 = \text{S}$ and reagent HS-Z in Scheme 21.

41

Scheme 29R = C₁-C₄ alkyl

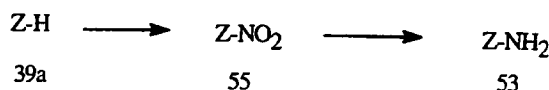
- Compounds of Formula 53 can be converted to compounds of Formulae 43, 48 or 52 via the diazonium compounds 54, by treatment with nitrous acid followed by subsequent reaction (Scheme 30). See reviews by Hegarty, pt. 2, pp 511-91 and Schank, pt. 2, pp 645-657, in Patai, "The Chemistry of Diazonium and Diazo Groups," Wiley, New York (1978). Treatment of Formula 54 compounds with cuprous halides or iodide ions yield compounds of Formula 43. Treatment of Formula 54 compounds with cuprous oxide in the presence of excess cupric nitrate provides compounds of Formula 48. (Cohen, Dietz, and Miser, *J. Org. Chem.*, (1977), 42, 2053). Treatment of Formula 54 compounds with (S₂)⁻² yields compounds of Formula 52.

Scheme 30

- Compounds of Formula 53 can be prepared from compounds of Formula 39a by nitration, followed by reduction (Scheme 31). A wide variety of nitrating agents is available (see Schofield, "Aromatic Nitration," Cambridge University Press, Cambridge (1980)). Reduction of nitro compounds can be accomplished in a number of ways (see March, *J. Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985),

pp 1103-4 and references therein). Formula 53 corresponds to Formula 13 in Scheme 6 when $Y^1 = NR^{15}$ and $R^{15} = H$.

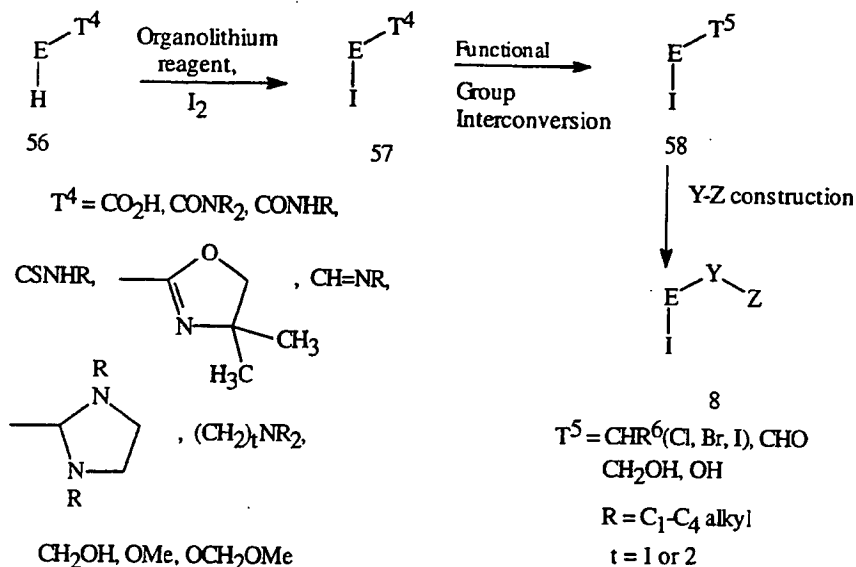
Scheme 31



- Iodides of Formula 8 can be prepared from compounds of Formula 58 by the methods described above in Schemes 21-25 for various Y-Z combinations. Compounds of Formula 58 can in turn be prepared from compounds of Formula 57 by functional group interconversions which are well known to one skilled in the art. The compounds of Formula 57 can be prepared by treating compounds of Formula 56 with an organolithium reagent such as *n*-BuLi or LDA followed by trapping the intermediate with iodine (Beak, P., Snieckus, V. *Acc. Chem. Res.*, (1982), 15, 306). Additionally, lithiation via halogen metal exchange of compounds of Formula 56, where H is replaced by Br, will produce an intermediate which can be trapped with iodine to prepare compounds of Formula 57 (Parham, W E, Bradsher, C. K. *Acc. Chem. Res.*, (1982), 15, 300 (Scheme 32).

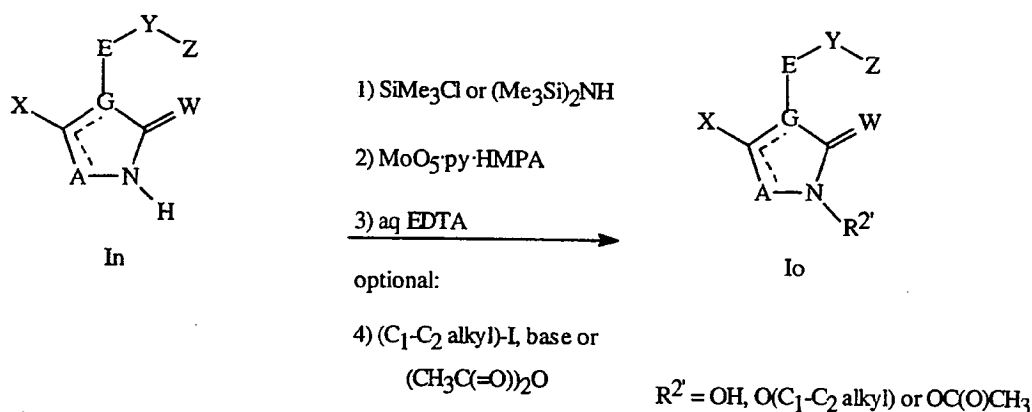
15

Scheme 32



- Conversion of compounds of Formula In to compounds of Formula Io is summarized in Scheme 33. Reaction of the secondary amides with silylating agents, such as trimethylsilyl chloride in the presence of base or hexamethyldisilazane in the presence of acid, provides the silylated intermediate which is oxidized *in situ* with the peroxo-molybdenum compound $\text{MoO}_5 \cdot \text{HMPA}$ complexed with pyridine or dimethylformamide. Subsequent hydrolysis with aqueous EDTA (ethylenediaminetetraacetic acid) liberates the hydroxylated amides (see S. A. Martin, P. G. Sammes and R. M. Upton, *J. Chem. Soc., Perkin Trans 1*, (1979), 2481 and J. H. Rigby and M. Qabar, *J. Org. Chem.* (1989), 54, 5852). Optional alkylation with $\text{C}_1\text{-C}_2$ alkyl halides in the presence of base or acylation with acetic anhydride can be performed on the hydroxyl amides of Formula Io where $\text{R}^{2'} = \text{OH}$.

Scheme 33



- It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula I may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences or functional group interconversions into the synthesis will aid in obtaining the desired products. The use and choice of the protecting groups will be apparent to one skilled in chemical synthesis (see, for example, Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991). One skilled in the art will recognize that, in some cases, after the introduction of a given reagent as it is depicted in any individual scheme, it may be necessary to perform additional routine synthetic steps not described in detail to complete the synthesis of compounds of Formula I. One skilled in the art will also recognize that it may be necessary to perform a combination of the steps illustrated in the above schemes in an

order other than that implied by the particular sequence presented to prepare the compounds of Formula I.

One skilled in the art will also recognize that compounds of Formula I and the intermediates described herein can be subjected to various electrophilic, nucleophilic, radical, organometallic, oxidation, and reduction reactions to add substituents or modify existing substituents.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except for chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated. ¹H NMR spectra are reported in ppm downfield from tetramethylsilane; s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, br s = broad singlet.

EXAMPLE 1

Step A: Preparation of methyl 3-isocyanato-2-thiophenecarboxylate

Diphosgene (4.6 mL) was added dropwise to a solution of methyl 3-amino-2-thiophenecarboxylate (5.0 g) in *p*-dioxane (100 mL) at room temperature under N₂. Triethylamine (5.3 mL) was then added with concomitant formation of a white precipitate. The resulting reaction mixture was heated at reflux overnight. The reaction was allowed to cool to room temperature and then filtered to remove solid impurities. The precipitate was rinsed with diethyl ether (about 250 mL) and the filtrate was concentrated under reduced pressure to yield 6.4 g of crude title compound of Step A as a brown solid. ¹H NMR (CDCl₃): δ 7.43 (d,1H), 6.78 (d,1H), 3.92 (s,3H).

Step B: Preparation of methyl 3-[[2,2-dimethylhydrazino]carbonyl]amino]-2-thiophenecarboxylate

The title compound of Step A (6.4 g) was dissolved in toluene (35 mL) under N₂ and the solution was cooled to about 5 °C (ice bath) followed by the subsequent addition of 1,1-dimethylhydrazine (2.7 mL). A beige precipitate formed immediately and the mixture was allowed to stir for 30 min. The solid was filtered off, rinsed with hexane and then dried under vacuum to afford 6.9 g (81%) of the title compound of Step B. ¹H NMR (CDCl₃): δ 10.66 (br s,1H), 8.05 (d,1H), 7.43 (d,1H), 5.49 (br s,1H), 3.89 (s,3H), 2.65 (s,6H).

Step C: Preparation of methyl 3-(3-chloro-4,5-dihydro-1-methyl-5-oxo-1H-1,2,4-triazol-4-yl)-2-thiophenecarboxylate

Triphosgene (16.8 g) was added to a solution of the title compound of Step B (6.9 g) in methylene chloride (250 mL) under N₂. The reaction mixture was heated at
5 reflux overnight, cooled, and then concentrated under reduced pressure. The resulting brown oil was dissolved in methylene chloride and washed with water. The aqueous layer was further extracted three times with methylene chloride and the combined organic extracts were dried (MgSO₄), filtered and concentrated *in vacuo* to yield 7.92 g
10 of the title compound of Step C. ¹H NMR (CDCl₃): δ 7.66 (d,1H), 7.13 (d,1H), 3.85 (s,3H), 3.52 (s,3H).

Step D: Preparation of methyl 3-(4,5-dihydro-3-methoxy-1-methyl-5-oxo-1H-1,2,4-triazol-4-yl)-2-thiophenecarboxylate

Sodium methoxide (16.5 mL of a 30% solution in methanol) was added to a solution of the title compound of Step C (7.9 g) in anhydrous dimethoxyethane/methanol
15 (85 mL/35 mL). The resulting yellow solution was heated to 50 °C for 2 h under N₂ and then left to stir overnight at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in methylene chloride. The resulting mixture was washed with water and then with saturated aqueous NaCl. The aqueous layer was filtered through Celite® and the filtrate was extracted three times with
20 methylene chloride. The combined methylene chloride layers were dried (MgSO₄), filtered, and concentrated under reduced pressure to give 5.4 g of an off-white solid. The crude product was purified by flash chromatography (20-100% ethyl acetate/hexane as eluent) to afford 3.9 g of the title compound of Step D as a white solid. ¹H NMR (CDCl₃): δ 7.58 (d,1H), 7.12 (d,1H), 3.93 (s,3H), 3.83 (s,3H), 3.44(s,3H).

25 Step E: Preparation of 2,4-dihydro-4-[2-(hydroxymethyl)-3-thienyl]-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a solution of the title compound of Step D (1.8 g) in methylene chloride (23 mL) under N₂ at -78 °C was added a solution of diisobutylaluminum hydride (18.3 mL, 1 M) in methylene chloride. The resulting solution was allowed to stir at
30 -78 °C for 15 min, warmed to room temperature and then stirred for 1.5 h. After cooling the reaction mixture to -78 °C, acetone was added and after about 10 min, the reaction mixture was quenched with 1N HCl. The reaction mixture was allowed to warm to room temperature, was diluted further with methylene chloride, and was then washed with water. The organic layer was dried (MgSO₄), filtered and concentrated *in vacuo* to
35 yield 1.3 g of the title compound of Step E as an off-white solid.

Step F: Preparation of 4-[2-(bromomethyl)-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a suspension of the title compound of Step E (2.6 g) in methylene chloride (20 mL) under N₂ at room temperature was added sequentially
5 triphenylphosphine (3.44 g) and carbon tetrabromide (5.58 g). The resulting orange solution was allowed to stir for 1 h at room temperature and was then concentrated under reduced pressure to give an orange oil. The residue was purified by flash chromatography (1:1 ethyl acetate:hexane as eluent) to afford 2.3 g of the title
10 compound of Step F, a compound of the invention, as a white solid. ¹H NMR (CDCl₃): δ 7.34 (d, 1H), 6.92 (d, 1H), 4.65 (s, 2H), 3.98 (s, 3H), 3.45 (s, 3H).

EXAMPLE 2

Step A: Preparation of 2-(3-bromophenyl)-2-methyl-1,3-dioxolane

1-(3-bromophenyl)ethanone (60.6 g), ethylene glycol (83.7 mL), and
p-toluenesulfonic acid (0.15 g) were dissolved in benzene (250 mL) and heated at reflux
15 overnight in a Dean-Stark apparatus. The mixture was cooled and washed with water. The aqueous layer was further extracted twice with chlorobutane and the combined organic layers were dried (MgSO₄), filtered and the solvent was removed under reduced pressure to yield 75.0 g of a yellow oil. The oil was purified by distillation under
20 reduced pressure (19-24 Pa, 64-74 °C) to afford 70.1 g of the title compound of Step A as an oil. ¹H NMR (CDCl₃): δ 7.64 (s, 1H), 7.40 (m, 2H), 7.20 (m, 1H), 4.0 (m, 2H), 3.7 (m, 2H), 1.63 (s, 3H).

Step B: Preparation of 2-[3-(trimethylsilyl)phenyl]-2-methyl-1,3-dioxolane

A three-neck flask was charged with magnesium pieces (2.0 g) and tetrahydrofuran (12 mL) under a nitrogen atmosphere. A small quantity of iodine was added and the
25 mixture turned yellow. To this yellow mixture was added dropwise a solution of the title compound of Step A (20.0 g) in 30 mL of THF. The reaction mixture was warmed to 65 °C during the addition and then was heated at reflux for 1.5 h after the addition was complete. After cooling the reaction to 60 °C, a solution of trimethylsilyl chloride (10.4 mL) in THF (12 mL) was added and the mixture was heated at reflux for two
30 hours and then was allowed to stir overnight at room temperature. The reaction mixture was poured into saturated aqueous NH₄Cl and the aqueous layer was extracted twice with diethyl ether and then once with ethyl acetate. The combined organic layers were dried over MgSO₄, filtered and the solvent was removed to give an oil (20.0 g) which crystallized upon standing. This solid was then recrystallized from pentane to afford
35 11.2 g of the title compound of Step B as a white solid melting at 54-55 °C. ¹H NMR

(CDCl₃): δ 7.63 (s,1H), 7.44 (m,2H), 7.33 (t,1H), 4.0 (m,2H), 3.78 (m,2H), 1.67 (s,3H), 0.27 (s,8H).

Step C: Preparation of 1-[3-(trimethylsilyl)phenyl]ethanone

To a solution of the title compound of Step B (11.2 g) in acetone (400 mL) was
5 added an aqueous solution of 1N hydrochloric acid (6 mL) and the mixture was heated at
reflux overnight. After cooling, the mixture was concentrated under reduced pressure
and the resulting residue was dissolved in diethyl ether and dried (MgSO₄). The drying
agent was removed by filtration and the solvent was removed under reduced pressure to
give a yellow oil. The crude product was combined with another batch of crude product
10 prepared in the same manner and purified by distillation (47 Pa, 58-59 °C) to afford 8.9 g
of the title compound of Step C as an oil. ¹H NMR (CDCl₃): δ 8.11 (s,1H), 7.92
(d,1H), 7.7 (d,1H), 7.47 (t,1H), 2.62 (s,3H), 0.30 (s,8H).

Step D: Preparation of 1-[3-(trimethylsilyl)phenyl]ethanone oxime

To a solution of the title compound of Step C (8.9 g) in methanol (120 mL)/water
15 (50 mL) was added sodium acetate (7.5 g) followed by the addition of hydroxylamine
hydrochloride (3.8 g). The mixture was heated at reflux overnight, cooled to room
temperature, and concentrated to an oil. The oil was mixed with water and extracted
three times with methylene chloride. The combined organic phases were dried (MgSO₄),
concentrated, and chromatographed on silica gel with 8% ethyl acetate/hexane to afford
20 the title compound of Step D as an oil. ¹H NMR (CDCl₃): δ 8.8 (br s,1H), 7.77 (s,1H),
7.5 (m,2H), 7.37 (t,1H), 2.31 (s,3H), 0.27 (s,8H).

Step E: Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3H-1,2,4-triazol-3-one

A solution of the title compound of Step D (1.6 g) in DMF (18 mL) was cooled to
25 0 °C (ice bath) under N₂. Sodium hydride (236 mg) was added and, after 20 min, a
solution of the title compound of Step F in Example 1 (2.3 g) in DMF (18 mL) was
added. The reaction mixture was kept at 0 °C for 1 h and then at room temperature for
another hour before quenching with water. The mixture was extracted four times with
30 ethyl acetate and the combined organic extracts were washed with saturated aqueous
NaCl, dried (MgSO₄), filtered and concentrated under reduced pressure to a gold oil.
The crude product was purified by flash chromatography (1:1 ethyl acetate:hexane as
eluent) to afford 2.7 g of the title compound of Step E, a compound of the invention, as
a very viscous oil/solid. ¹H NMR (CDCl₃): δ 7.76 (s,1H), 7.60 (m,1H), 7.54 (m,1H),
35 7.36 (d,1H), 7.32 (d,1H), 6.94 (d,1H), 5.29 (s,2H), 3.89 (s,3H), 3.41 (s,3H), 2.21
(s,3H), 0.28 (s,9H).

EXAMPLE 3Preparation of 4-[2-[(2,5-dimethylphenoxy)methyl]-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a solution of the title compound of Step E in Example 1 (200 mg),
5 2,5-dimethylphenol (152 mg) and triphenylphosphine (261 mg) in THF (2 mL) at 0 °C (ice bath) under N₂ was added diethyl azodicarboxylate (231 mg). The ice bath was removed and the reaction mixture warmed to room temperature. After stirring for 4 h at room temperature, the reaction mixture was concentrated under reduced pressure to give an orange oil. Purification of this orange oil by flash chromatography (1:1 ethyl
10 acetate:hexane eluent) followed by preparative TLC (10% ethyl acetate/methylene chloride) afforded 100 mg of the title compound of Example 3, a compound of the invention, as yellow-brown solid melting at 151-153 °C. ¹H NMR (CDCl₃): δ 7.34 (d,1H), 7.01 (d,1H), 6.95 (d,1H), 6.68 (m,2H), 5.15 (s,2H), 3.94 (s,3H), 3.43 (s,3H), 2.30 (s,3H), 2.16 (s,3H).

15

EXAMPLE 4Step A: Preparation of 3-(1,5-dihydro-3-methoxy-1-methyl-5-oxo-4H-1,2,4-triazol-4-yl)-2-thiophenecarboxaldehyde

A solution of 4-methylmorpholine N-oxide (0.38 g, 0.0033 mol) in dichloromethane (7 mL) was stirred over anhydrous magnesium sulfate for 15 minutes
20 and then filtered. Molecular sieves (4Å) were added to the filtrate, followed by tetrapropylammonium perruthenate (0.11 g, 0.0003 mol). A solution of the title compound of Step E in Example 1 (0.39 g, 0.0016 mol) in dichloromethane (1 mL) was added and the resulting mixture was stirred at room temperature for 1 hr. The reaction mixture was diluted with diethyl ether (10 mL), filtered through a short plug of silica gel,
25 and the filtrate was concentrated by rotary evaporation to give 0.21 g of the title compound of Step A as a pale solid. ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s,1H), 7.79 (d,1H, J = 5.2 Hz), 7.16 (d,1H, J = 5.2 Hz), 4.01 (s,3H), 3.46 (s,3H).

Step B: Preparation of (1,1-dimethylethyl) dichloro(diethoxyphosphinyl)acetate

A solution of 5.25% sodium hypochlorite (Clorox® bleach; 421.5 g, 0.2973 mol) was adjusted to pH 7.1 with 3N HCl. *tert*-Butyl diethylphosphonoacetate (15.0 g, 0.0595 mol) was added dropwise at 0 °C with vigorous stirring. After complete addition, the ice bath was removed and stirring was continued for 1 h. The reaction mixture was extracted five times with hexane and the combined organic phases were dried (MgSO₄), filtered and concentrated to afford 18.4 g of the title compound of
35 Step B as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 4.41-4.36 (m,4H), 1.57 (s,9H), 1.40 (t,6H, J = 7.2 Hz).

Step C: Preparation of (1,1-dimethylethyl) chloro(diethoxyphosphinyl)acetate

The title compound of Step B (18.4 g, 0.0572 mol) was dissolved in ethanol (140 mL) and cooled to 0 °C. A solution of sodium sulfite (14.4 g, 0.1144 mol) in H₂O (63 mL) was added with stirring such that the internal temperature remained below 14 °C. The cooling bath was removed and the mixture was stirred at room temperature for 30 min. The reaction mixture was extracted five times with chloroform, and the combined organic phase was dried (MgSO₄), filtered and concentrated to afford 16.4 g of the title compound of Step C as a clear oil. ¹H NMR (300 MHz, CDCl₃): δ 4.43 (d, 1H, J = 15.9 Hz), 4.30-4.24 (m, 4H), 1.52 (s, 9H), 1.38 (t, 6H, J = 6.9 Hz).

Step D: Preparation of (1,1-dimethylethyl) 2-chloro-3-[3-(1,5-dihydro-3-methoxy-1-methyl-5-oxo-4H-1,2,4-triazol-4-yl)-2-thienyl]-2-propenoate

A solution of the title compound of Step C (0.026 g, 0.0009 mol) in ethyl acetate (2 mL) was added to a mixture of calcium hydroxide (0.068 g, 0.0009 mol) and the title compound of Step A (0.220 g, 0.0009 mol) in ethyl acetate (5 mL). The resulting mixture was stirred at 60 °C overnight. Three additional 0.026 g (0.0009 mol) portions of the title compound of Step C were added at 3 h intervals and then the temperature of the mixture was increased to 70 °C and heating was continued overnight. After 40 h of total reaction time, the reaction mixture was poured into ice water and extracted three times with ethyl acetate. The combined organic phase was washed successively with saturated aqueous NaCl and then with a 1/1 mixture of saturated aqueous NaCl and saturated aqueous sodium hydrogen carbonate, dried (Na₂SO₄), filtered and concentrated to a pale yellow oil. The crude product was purified by flash column chromatography on silica gel to give a preliminary fraction of 0.170 g of the title compound of Step D, a compound of the invention, as a white solid (m.p. 105-115 °C) consisting of a 7:3 ratio of *Z*- and *E*-isomers, respectively, followed by a final fraction of 0.04 g of the title compound of Step D, a compound of the invention, as a white solid (m.p. 104 °C) consisting of a 5:1 ratio of *Z*- and *E*-isomers, respectively. ¹H NMR (300 MHz, CDCl₃; for the *Z/E* mixture): δ 7.77 and 7.00 (2d, 1H total, J = 0.8 Hz), 7.62 and 7.46 (2dd, 1H total, J = 0.8, 5.4 Hz), 7.09 and 6.98 (2dd, 1H total, J = 0.9, 5.4 Hz), 3.97 (s, 3H), 3.45 (s, 3H), 1.54 (s, 9H).

EXAMPLE 5

Step A: Preparation of monomethyl 3,4-furandicarboxylate

A solution of NaOH (5.0 g) in H₂O/methanol (20 mL/60 mL) was added to a solution of dimethyl 3,4-furandicarboxylate (23 g) in methanol (250 mL) at 0 °C. The mixture was allowed to stir at 0 °C for 2 h, and then was warmed to room temperature and left to stir overnight. The congealed mixture was concentrated under reduced

pressure and the resulting solid was dissolved in water. The aqueous solution was extracted three times with diethyl ether and the combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure to afford a white solid (3.5 g) which was the starting dimethyl 3,4-furandicarboxylate. The remaining aqueous
5 layer was acidified by dropwise addition of concentrated HCl and extracted three times with methylene chloride. The combined methylene chloride extracts were dried (MgSO_4), filtered and concentrated under reduced pressure to afford 22.97 g of the title compound of Step A as a white solid. ^1H NMR (CDCl_3): δ 13.02 (br s, 1H), 8.25 (d, 1H), 8.13 (d, 1H), 4.00 (s, 3H).

10 Step B: Preparation of methyl 4-(azidocarbonyl)-3-furancarboxylate

To a solution of the title compound of Step A (23 g), triethylamine (18.8 mL) and DMF (120 mL) at 0 °C under nitrogen was added a solution of diphenylphosphorylazide (29.1 mL) in DMF (20 mL) via an addition funnel. The reaction was allowed to stir for 3 h at 0 °C and was monitored by TLC (1:1 ethyl
15 acetate/hexane). The reaction mixture was poured onto an ice/diethyl ether mixture and then extracted three times with diethyl ether. The combined organic extracts were washed with a 10% aqueous NaHCO_3 solution, dried (MgSO_4) and concentrated to give 24 g of crude product, the title compound of Step B, as an oil/solid mixture.

20 Step C: Preparation of methyl 4-[(2,2-dimethylhydrazino)carbonyl]amino]-3-furancarboxylate

A solution of the title compound of Step B (24 g) in toluene (200 mL) was heated at 70 °C for 3 h and then at 90 °C for another 3 h. The reaction was followed by IR. After cooling to 0 °C, 1,1-dimethylhydrazine (9.4 mL) was added and the reaction was allowed to stir overnight at room temperature. The resulting precipitate was
25 collected by filtration to afford 13.5 g of the title compound of Step C as a white solid melting at 138-139 °C. The filtrate was concentrated under reduced pressure to give a second batch, 15.7 g of crude product, the title compound of Step C, as an orange solid. ^1H NMR (CDCl_3): δ 9.28 (br s, 1H), 8.03 (d, 1H), 7.85 (d, 1H), 5.44 (d, 1H), 3.88 (s, 3H), 2.62 (s, 6H).

30 Step D: Preparation of methyl 4-(3-chloro-1,5-dihydro-1-methyl-5-oxo-4H-1,2,4-triazol-4-yl)-3-furancarboxylate

Triphosgene (40.1 g) was added to a solution of crude title compound of Step C (15.4 g) in methylene chloride (550 mL) at 0 °C. The mixture was heated at reflux for 4 h, cooled to room temperature and stirred overnight. The reaction mixture was
35 concentrated to a brown oil which was dissolved in methylene chloride, washed with water and the aqueous layer extracted three times with methylene chloride. The

combined organic extracts were dried (MgSO₄), filtered and concentrated to a brown oil. Purification by flash chromatography (1:1 hexane:ethyl acetate) provided 5.34 g of the title compound of Step D as a yellow solid melting at 129-130 °C. ¹H NMR (CDCl₃): δ 8.10 (d,1H), 7.72 (d,1H), 3.80 (s,3H), 3.52 (s,3H).

5 Step E: Preparation of methyl 4-(1,5-dihydro-3-methoxy-1-methyl-5-oxo-4H-1,2,4-triazol-4-yl)-3-furancarboxylate

A solution of sodium methoxide (11.4 mL, 30% in methanol) was added to a solution of the title compound of Step D (5.34 g) in methanol/dimethoxyethane (26 mL/26 mL) while stirring under nitrogen. The yellow solution was heated to 40 °C
10 for 5 h, cooled to room temperature and left to stir overnight under nitrogen. The reaction mixture was poured into saturated aqueous NH₄Cl (50 mL) and the resulting mixture was extracted three times with ethyl acetate. The combined organic extracts were dried (MgSO₄), filtered and concentrated to a yellow solid. The yellow solid was dried under vacuum to afford 4.7 g of the title compound of Step E melting at
15 131-133 °C. ¹H NMR (CDCl₃): δ 8.04 (d,1H), 7.68 (d,1H), 3.94 (s,3H), 3.78 (s,3H), 3.43 (s,3H).

Step F: Preparation of 2,4-dihydro-4-[4-(hydroxymethyl)-3-furanyl]-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

A solution of the title compound of Step E (4.6 g) in methylene chloride (40 mL)
20 under nitrogen was cooled to -78 °C while stirring. A solution of diisobutylaluminum hydride (55.0 mL, 1 M in CH₂Cl₂) in methylene chloride was then added, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction was monitored by TLC (5% methanol/ethyl acetate). After cooling back down to -78 °C, the reaction was diluted with acetone (45 mL), quenched with glacial acetic acid (20 mL)
25 and then allowed to warm to room temperature. The resulting mixture was further diluted with water (200 mL) and extracted successively with methylene chloride and ethyl acetate. The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to yield 3.62 g of the title compound of Step F as an orange solid melting at 132.5-133.5 °C. ¹H NMR (CDCl₃): δ 7.53 (s,2H), 4.38
30 (s,3H), 3.99 (s,3H), 3.44 (s,3H).

Step G: Preparation of 4-[4-(bromomethyl)-3-furanyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a solution of the title compound of Step F (3.6 g), and triphenylphosphine (5.1 g) in methylene chloride(40 mL) under N₂ at 0 °C was added carbon
35 tetrabromide(8.0 g). The resulting orange solution was allowed to stir overnight at room temperature and then was concentrated under reduced pressure to give a brown oil. The

residue was purified by flash chromatography (1:2 ethyl acetate : hexane as eluent) to afford 3.6 g (78%) of the title compound of Step G, a compound of the invention, as a white solid melting at 147-149 °C.

EXAMPLE 6

5 Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[4-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]-3-furanyl]-3H-1,2,4-triazol-3-one

A solution of the title compound of Step D in Example 2 (180 mg) in DMF (2 mL) under N₂ was cooled to 0 °C. Sodium hydride (27 mg, 95%) was added and the mixture was stirred at 0 °C for 20 min. A solution of the title compound of Step G in
10 Example 5 (250 mg) in DMF (2 mL) was added via syringe and the resulting mixture was allowed to warm to room temperature. The mixture was left to stir overnight at room temperature. The reaction mixture was cooled to 0 °C, quenched with water and extracted three times with methylene chloride. The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to a yellow oil. The oil
15 was purified by flash chromatography (1:2 ethyl acetate : hexane as eluent) to afford 242 mg of the title compound of Example 6, a compound of the invention, as a clear oil. ¹H NMR (CDCl₃): δ 7.70 (s,1H), 7.54 (m,4H), 7.34 (t,1H), 5.11 (s,2H), 3.86 (s,3H), 3.32 (s,3H), 2.14 (s,3H), 0.28 (s,9H).

EXAMPLE 7

20 Step A: Preparation of 3,4-dihydro-7-methoxy-N-(phenylmethyl)-1-naphthalenamine

A mixture containing 7-methoxytetralone (25.0 g), benzylamine (15.8 mL), toluene and 4Å molecular sieves (42.0 g) was heated at reflux for 3.5 h. The mixture was cooled to room temperature, filtered through a layer of Florisil® and concentrated
25 under reduced pressure to yield 42.1 g of crude title compound of Step A.

Step B: Preparation of 7-methoxy-1-naphthalenamine

To a solution of crude title compound of Step A (42.1 g) in diphenyl ether (320 mL) was added 10% palladium on carbon (17.8 g). The heterogeneous black mixture was heated at reflux for 5 h under N₂ while stirring. The reaction mixture was
30 allowed to cool to room temperature and filtered. The filtrate was acidified with concentrated HCl and the resulting white precipitate was collected by filtration, washed with CH₂Cl₂, dissolved in water and treated with 50% aqueous NaOH until basic. The aqueous mixture was then extracted four times with CH₂Cl₂. The combined organic extracts were dried (MgSO₄), filtered and the filtrate was concentrated under reduced
35 pressure to give 20.9 g of the title compound of Step B as a pink solid melting at

79-80 °C. ¹H NMR (CDCl₃): δ 7.70 (d,1H), 7.29-7.13 (m,3H), 7.07 (d,1H), 6.80 (dd,1H), 4.0 (br s,2H), 3.94 (s,3H).

Step C: Preparation of 1-isocyanato-7-methoxynaphthalene

To a solution of the title compound of Step B (5.0 g) in *p*-dioxane (115 mL) at room temperature was added via syringe diphosgene (4.2 mL) followed by the addition of triethylamine (4.8 mL). The mixture was heated at reflux overnight while stirring. The reaction was monitored by IR (2267 cm⁻¹). The reaction mixture was filtered and the residue was washed with diethyl ether. The filtrate was concentrated under reduced pressure to give 5.8 g of the title compound of Step C as a beige solid which was used without further purification.

Step D: Preparation of *N*-(7-methoxy-1-naphthalenyl)-2,2-dimethylhydrazinecarboxamide

A solution of crude title compound of Step C (5.8 g) in toluene (85 mL) was cooled to 0 °C under N₂. While stirring the reaction solution, 1,1-dimethylhydrazine (2.5 mL) was added and the mixture was allowed to warm to room temperature. After stirring for 30 min at room temperature, a precipitate formed. Filtration afforded 5.1 g of the title compound of Step D as a white solid melting at 152-153 °C. ¹H NMR (CDCl₃): δ 8.48 (br s,1H), 7.89 (d,1H), 7.77 (m,1H), 7.58 (d,1H), 7.34 (t,1H), 7.17 (m,2H), 5.72 (br s,1H), 3.93 (s,3H), 2.72 (s,6H).

Step E: Preparation of 5-chloro-2,4-dihydro-4-(7-methoxy-1-naphthalenyl)-2-methyl-3*H*-1,2,4-triazol-3-one

A solution of triphosgene (16.7 g) in ethyl acetate (130 mL) was heated to reflux and a suspension of the title compound of Step D (4.9 g) in ethyl acetate was added via cannula and the aid of a mechanical pump over a period of 40 min. The temperature was held at approximately 75 °C during the addition. After the addition was complete, the reaction mixture was heated at reflux for 2 h, cooled to room temperature and stirred overnight at room temperature. The reaction mixture was poured into a solution of saturated aqueous sodium bicarbonate, extracted with ethyl acetate, and the combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure to afford 4.9 g of the title compound of Step E as a white solid melting at 142-143 °C. ¹H NMR (CDCl₃): δ 7.93 (dd,1H), 7.84 (d,1H), 7.43 (m,2H), 7.24 (dd,1H), 6.75 (d,1H), 3.87 (s,3H), 3.62 (s,3H).

Step F: Preparation of 5-chloro-2,4-dihydro-4-(7-hydroxy-1-naphthalenyl)-2-methyl-3*H*-1,2,4-triazol-3-one

A solution of the title compound of Step E (2.9 g) in methylene chloride (35 mL) was cooled to 0 °C while stirring under N₂, and aluminum trichloride (4.0 g) was added

in portions. The reaction mixture was allowed to warm to room temperature and then was heated to reflux for 18 h. The reaction mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography (1:4 ethyl acetate : hexane as eluent) to afford 2.2 g of the title compound of Step F. ^1H NMR ($\text{Me}_2\text{SO}-d_6$): δ 10.08 (s,1H), 8.02 (d,1H), 7.95 (d,1H), 7.59 (dd,1H), 7.41 (t,1H), 7.18 (dd,1H), 6.71 (d,1H), 3.49 (s,3H).

Step G: Preparation of 2,4-dihydro-4-(7-hydroxy-1-naphthalenyl)-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a solution of the title compound of Step F (3.3 g) in THF (38 mL) was added a solution of sodium methoxide (6.5 mL, 30% in methanol) while stirring under N_2 . The mixture was heated at 50 °C for 6 h and cooled to room temperature and left to stir overnight. The reaction was quenched with water and extracted three times with methylene chloride and then three times with ethyl acetate. The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. Trituration (ethyl acetate : hexane 1:1) of the crude product provided 1.61 g of the title compound of Step G as a light brown solid melting at greater than 250 °C. ^1H NMR ($\text{Me}_2\text{SO}-d_6$): δ 10.00 (s,1H), 7.93 (m,2H), 7.47 (dd,1H), 7.36 (t,1H), 7.15 (dd,1H), 6.73 (d,1H), 3.86 (s,3H), 3.39 (s,3H).

Step H: Preparation of 5-chloro-3-[4-(trifluoromethyl)phenyl]-1,2,4-thiadiazole

A mixture of 4-(trifluoromethyl)benzamidinium hydrochloride dihydrate (5.0 g), water (50 mL), methylene chloride (100 mL), benzyltriethylammonium chloride (0.44 g), and perchloromethyl mercaptan (2.1 mL) was prepared at room temperature and then cooled to 0 °C. A solution of sodium hydroxide (3.07 g) in water (50 mL) was added via an addition funnel while maintaining the temperature below 10 °C. The reaction was left to stir overnight at room temperature. The mixture was transferred to a separatory funnel and the two layers were separated. The organic layer was washed with saturated sodium bicarbonate, dried (MgSO_4), filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography (hexane as eluent) to afford 3.7 g of the title compound of Step H as a white powder. ^1H NMR (CDCl_3): δ 8.36 (d,2H), 7.73 (d,2H).

Step I: Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[7-[[3-[4-(trifluoromethyl)phenyl]-1,2,4-thiadiazol-5-yl]oxy]-1-naphthalenyl]-3H-1,2,4-triazol-3-one

A solution of the title compound of Step G (214 mg) and the title compound of Step H (251 mg) in DMF (5 mL) was cooled to 0 °C under N_2 . To the resulting yellow

- solution was added sodium hydride (25 mg) and the mixture was left to stir overnight at room temperature. The reaction was then cooled to 0 °C, quenched with water and extracted twice with ethyl acetate. The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The crude yellow solid was purified by crystallization in methanol to afford 216 mg of the title compound of Step I, a compound of the invention as a white powder melting at 216-217 °C. ¹H NMR (Me₂SO-*d*₆): δ 8.30 (m,3H), 8.23 (dd,1H), 7.98 (d,1H), 7.91-7.81 (m,3H), 7.73 (m,2H), 3.86 (s,3H), 3.33 (s,3H).

EXAMPLE 8

- 10 Step A: Preparation of 3-nitro-2-(3-phenoxyphenoxy)pyridine

- 3-Phenoxyphenol (3 g, 16.1 mmol) was added to a solution of potassium *t*-butoxide (1.90 g of 90 %, 16.6 mmol) in 50 mL of dry tetrahydrofuran at room temperature after which the reaction was stirred at room temperature for 10 min. Then, 2-chloro-3-nitropyridine (2.56 g, 16.1 mmol) was added. The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure. The residue was diluted with water, extracted twice with methylene chloride and dried over magnesium sulfate. The solvent was then removed to yield the title compound of Step A as an oil. ¹H NMR (CDCl₃; 300 MHz): δ 6.85 (m,1H), 6.90 (m,2H), 7.0-7.2 (m,4H), 7.3-7.4 (m,3H), 8.35 (m,2H).

- 20 Step B: Preparation of 3-isocyanato-2-(3-phenoxyphenoxy)pyridine

- A solution of the entire amount of the intermediate in Step A and 6 mL water in 60 mL acetic acid was heated on a steam bath to 65 °C and at this temperature iron powder (3.05 g, 54.6 mmol) was added portionwise noting the exotherm after each addition. The reaction temperature was kept between 65-85 °C by the addition rate and by a water cooling bath. After stirring for an additional 10 min at 85 °C, the reaction was cooled to room temperature, diluted with methylene chloride and filtered through Celite®. The filtrate was washed once with water, then once with saturated sodium bicarbonate, and dried over magnesium sulfate. The solvent was then removed under reduced pressure to yield an oil. This intermediate oil was then dissolved in 60 mL of dry toluene and to this solution was added diphosgene (3.29 g, 16.6 mmol). The mixture was then refluxed with a water scrubber in place for 4 h. The reaction was cooled to room temperature, concentrated under reduced pressure to give crude title compound of Step B as solids which were used entirely in the next reaction (Step C).

Step C: Preparation of 5-chloro-2,4-dihydro-2-methyl-4-[2-(3-phenoxyphenoxy)-3-pyridinyl]-3H-1,2,4-triazol-3-one

The solids from Step B were dissolved in 100 mL of dry tetrahydrofuran. 1,1-Dimethylhydrazine (3 g, 50.0 mmol) was added and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure. The residue was diluted with water and extracted twice with diethyl ether. The combined organic layers were then washed once with saturated aqueous NaCl solution and dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oil. This oil was then dissolved in 200 mL methylene chloride and cooled to 0 °C at which temperature triphosgene (4.08 g, 13.7 mmol) was added. The reaction mixture was refluxed for 16 h, cooled to room temperature and washed once with water. The organic layer was then dried over magnesium sulfate and concentrated under reduced pressure to yield a crude oil which was purified by silica gel chromatography using 3:2/hexanes:ethyl acetate as the eluent to yield 2 g of the title compound of Step C, a compound of the invention, as a solid. ¹H NMR (CDCl₃; 300 MHz): δ 3.53 (s,3H), 6.8-6.9 (m,3H), 7.0-7.2 (m,4H), 7.3-7.4 (m,3H), 7.71 (dd,1H, J=1.9, 7.7Hz), 8.27 (dd,1H, J=1.8, 4.9Hz).

EXAMPLE 9

Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[2-(3-phenoxyphenoxy)-3-pyridinyl]-3H-1,2,4-triazol-3-one

The title compound of Step C in Example 8 (2 g, 5.26 mmol) was dissolved in 100 mL of methanol and to this solution was added sodium methoxide (1.90 g 30% solution in methanol, 10.5 mmol) at room temperature. The reaction was subsequently refluxed for 6 h, cooled to room temperature and concentrated under reduced pressure to semisolids. The semisolids were diluted with water, extracted twice with methylene chloride and dried over magnesium sulfate. The solvent was removed under reduced pressure to yield an oil which was subsequently purified by silica gel chromatography using 1:2/hexanes:ethyl acetate as the eluent to yield 0.90 g of the title compound of Step D, compound of the invention, as a solid melting at 113-114 °C ¹H NMR (CDCl₃; 400 MHz): δ 3.44 (s,3H), 3.91 (s,3H), 6.80 (m,1H), 6.85 (m,2H), 7.06 (dd,2H, J=1.1, 8.6 Hz), 7.12 (dd,2H, J=4.9, 7.6Hz), 7.3-7.4 (m,3H), 7.71 (dd,1H, J=1.8, 7.6Hz), 8.21 (dd,1H, J=1.9, 4.9Hz).

EXAMPLE 10**2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[3-[4-(trifluoromethyl)phenyl]-1,2,4-thiadiazol-5-yl]oxy]methyl]-3-thienyl]-3H-1,2,4-triazol-3-one**

A solution of the title compound of Step E in Example 1 (250 mg) and the title compound of Step H in Example 7 (329 mg) in DMF (5 mL) was cooled to 0 °C under N₂. To the resulting yellow solution was added sodium hydride (32 mg) and the mixture was left to stir overnight at room temperature. The reaction mixture was poured into water and extracted three times with CH₂Cl₂. The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting crude yellow solid was purified by crystallization in hexane : ethyl acetate (1:1) to afford 191 mg of the title compound of Example 10, a compound of the invention, as a white powder melting at 138-139 °C. ¹H NMR (CDCl₃): δ 8.29 (d,2H), 7.71 (d,2H), 7.44 (d,1H), 6.98 (d,1H), 5.75 (s,2H), 3.91 (s,3H), 3.43 (s,3H).

By the procedures described herein together with methods known in the art, the following compounds of Tables 1 to 21 can be prepared. The following abbreviations are used in the Tables which follow: *t* = tertiary, *s* = secondary, *n* = normal, *i* = iso, *c* = cyclo, Me = methyl, Et = ethyl, Pr = propyl, *i*-Pr = isopropyl, Bu = butyl, Ph = phenyl, nap = naphthalenyl, MeO = methoxy, EtO = ethoxy, PhO = phenoxy, MeS = methylthio, EtS = ethylthio, CN = cyano, NO₂ = nitro, TMS = trimethylsilyl, S(O)Me = methylsulfinyl, and S(O)₂Me = methylsulfonyl.

TABLE 1

Compounds of Formula I where A = N, G = N, W = O, X = OMe, R² = Me, Y = CH₂O-N=C(Me), Z = 3-CF₃-Ph, the floating double bond is attached to A and

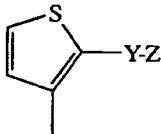
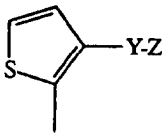
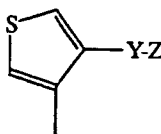
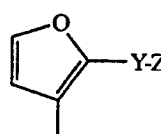
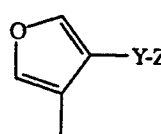
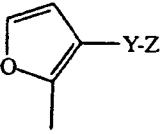
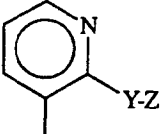
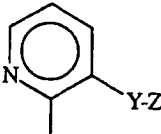
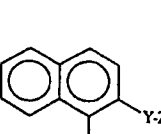
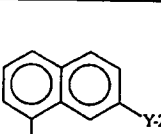
E-Y-Z	E-Y-Z	E-Y-Z	E-Y-Z	E-Y-Z
				
				

TABLE 2

Compounds of Formula I where A = O, G = C, W = O, X = OMe, R² = Me,
Y = CH₂O-N=C(Me), Z = 3-CF₃-Ph, the floating double bond is attached to G and

E-Y-Z	E-Y-Z	E-Y-Z	E-Y-Z	E-Y-Z

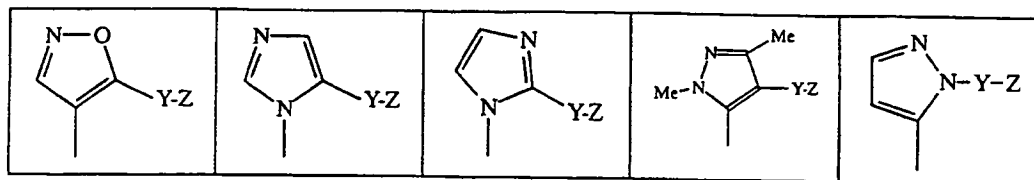
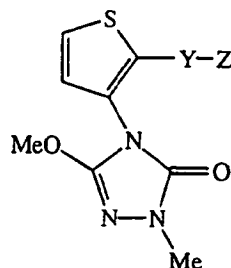


TABLE 3

Compounds of Formula I defined as:

 $Z = 3\text{-CF}_3\text{-Ph}$

Y	Y	Y	Y
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

Z = 3-Me₃Si-Ph

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(<i>c</i> -Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(<i>c</i> -Pr)=N

Z = 4-CF₃-2-pyridinyl

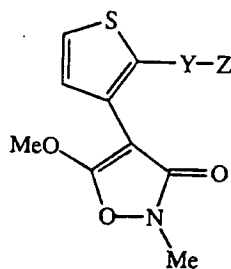
<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(<i>c</i> -Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)

61

CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

TABLE 4

Compounds of Formula I defined as:

Z = 3-CF₃-Ph

Y	Y	Y	Y
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH=N-O
C(Me)=C(Me)	CH ₂ O	CH(Me)S	C(=O)
S(O) ₂	CH=C(Cl)C(=O)O	O	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	N=C(Cl)C(=O)O
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ OC(=S)N(Me)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ O-N=C(Me)OCH ₂
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ N(Me)-N=C(Me)
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ OC(=S)S
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ SC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ OC(Me)=C(CN)
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	C(Me)=N-O
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	

O-N=CH S(O)	O-N=C(Me) CH ₂ SC(Et)=N	CH=N-N=C(Me) C≡C-C(=O)O	C≡C CH ₂ SC(c-Pr)=N
----------------	---------------------------------------	----------------------------	-----------------------------------

Z = 3-Me₃Si-Ph

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

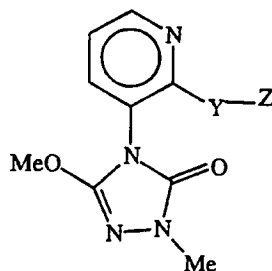
Z = 4-CF₃-2-pyridinyl

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)

CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

TABLE 5

Compounds of Formula I defined as:

Z = 3-CF₃-Ph

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S

CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

Z = 3-Me₃Si-Ph

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

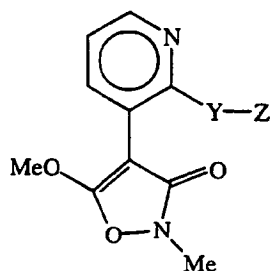
Z = 4-CF₃-2-pyridinyl

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O

$S(O)_2$	$CH=C(Cl)C(=O)O$	O	$C(=O)$
$CH_2O-N=C(CN)$	$CH=N-O-CH_2$	$CH_2OC(=O)NH$	$CH_2O-N=C(SMe)$
$CH_2O-N=C(c-Pr)$	$CH=N-O-CH(Me)$	$CH_2O-N=C(OMe)$	$N=C(Cl)C(=O)O$
$CH_2O-N=C(CN)C(=O)$	$CH_2O-N=C(Et)$	$CH_2O-N=C(Cl)$	$CH_2O-N=C(CF_3)$
$CH_2O-N=C(NHMe)$	$CH_2O-N=C(NH_2)$	$CH_2OC(=S)NH$	$CH_2OC(=S)N(Me)$
$CH_2O-N(Me)C(=O)N(Me)$	$CH_2O-N(Me)C(=S)N(Me)$	$CH_2O-N=C(Me)N(Me)$	$CH_2O-N=C(Me)OCH_2$
$CH_2SC(SMe)=N$	$CH=N-N(Me)$	$CH_2O-N=C(Me)N=N$	$CH_2N(Me)-N=C(Me)$
$CH_2OC(=O)O$	$CH_2OC(=S)O$	$CH_2OC(=O)S$	$CH_2OC(=S)S$
$CH_2SC(=O)N(Me)$	$CH_2SC(=O)NH$	$CH_2SC(=S)N(Me)$	$CH_2SC(=S)S$
$CH_2SC(=O)O$	$CH_2SC(=S)O$	$CH_2SC(=O)S$	$CH_2O-N=C(SMe)CH_2O$
$CH_2SC(=NMe)S$	$CH_2N(Me)C(=O)N(Me)$	$CH_2O-N=C(Me)CH_2O$	$CH_2OC(Me)=C(CN)$
$CH_2O-N=C(Me)CH_2S$	$CH_2O-N=C(SMe)CH_2S$	$OCH_2CH_2O-N=C(Me)$	$C(Me)=N-O$
$O-N=CH$	$O-N=C(Me)$	$CH=N-N=C(Me)$	$C\equiv C$
$S(O)$	$CH_2SC(Et)=N$	$C\equiv C-C(=O)O$	$CH_2SC(c-Pr)=N$

TABLE 6

Compounds of Formula I defined as:

 $Z = 3-CF_3-Ph$

Y	Y	Y	Y
S	CH_2CH_2	$CH(Me)O$	SCH_2
$CH=CH$	$CH(Me)CH_2$	OCH_2	$SCH(Me)$
$C(Me)=CH$	$CH_2CH(Me)$	$OCH(Me)$	$CH_2O-N=CH$
$CH=C(Me)$	$CH(Me)CH(Me)$	CH_2S	
$C(Me)=C(Me)$	CH_2O	$CH(Me)S$	$CH=N-O$
$S(O)_2$	$CH=C(Cl)C(=O)O$	O	$C(=O)$
$CH_2O-N=C(CN)$	$CH=N-O-CH_2$	$CH_2OC(=O)NH$	$CH_2O-N=C(SMe)$
$CH_2O-N=C(c-Pr)$	$CH=N-O-CH(Me)$	$CH_2O-N=C(OMe)$	$N=C(Cl)C(=O)O$
$CH_2O-N=C(CN)C(=O)$	$CH_2O-N=C(Et)$	$CH_2O-N=C(Cl)$	$CH_2O-N=C(CF_3)$
$CH_2O-N=C(NHMe)$	$CH_2O-N=C(NH_2)$	$CH_2OC(=S)NH$	$CH_2OC(=S)N(Me)$

CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

Z = 3-Me₃Si-Ph

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)
C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

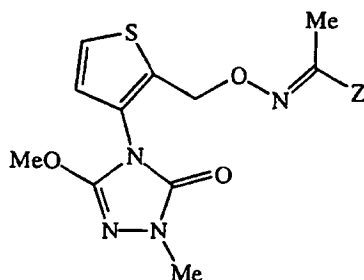
Z = 4-CF₃-2-pyridinyl

<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
S	CH ₂ CH ₂	CH(Me)O	SCH ₂
CH=CH	CH(Me)CH ₂	OCH ₂	SCH(Me)

C(Me)=CH	CH ₂ CH(Me)	OCH(Me)	CH ₂ O-N=CH
CH=C(Me)	CH(Me)CH(Me)	CH ₂ S	CH ₂ O-N=C(Me)
C(Me)=C(Me)	CH ₂ O	CH(Me)S	CH=N-O
S(O) ₂	CH=C(Cl)C(=O)O	O	C(=O)
CH ₂ O-N=C(CN)	CH=N-O-CH ₂	CH ₂ OC(=O)NH	CH ₂ O-N=C(SMe)
CH ₂ O-N=C(c-Pr)	CH=N-O-CH(Me)	CH ₂ O-N=C(OMe)	N=C(Cl)C(=O)O
CH ₂ O-N=C(CN)C(=O)	CH ₂ O-N=C(Et)	CH ₂ O-N=C(Cl)	CH ₂ O-N=C(CF ₃)
CH ₂ O-N=C(NHMe)	CH ₂ O-N=C(NH ₂)	CH ₂ OC(=S)NH	CH ₂ OC(=S)N(Me)
CH ₂ O-N(Me)C(=O)N(Me)	CH ₂ O-N(Me)C(=S)N(Me)	CH ₂ O-N=C(Me)N(Me)	CH ₂ O-N=C(Me)OCH ₂
CH ₂ SC(SMe)=N	CH=N-N(Me)	CH ₂ O-N=C(Me)N=N	CH ₂ N(Me)-N=C(Me)
CH ₂ OC(=O)O	CH ₂ OC(=S)O	CH ₂ OC(=O)S	CH ₂ OC(=S)S
CH ₂ SC(=O)N(Me)	CH ₂ SC(=O)NH	CH ₂ SC(=S)N(Me)	CH ₂ SC(=S)S
CH ₂ SC(=O)O	CH ₂ SC(=S)O	CH ₂ SC(=O)S	CH ₂ O-N=C(SMe)CH ₂ O
CH ₂ SC(=NMe)S	CH ₂ N(Me)C(=O)N(Me)	CH ₂ O-N=C(Me)CH ₂ O	CH ₂ OC(Me)=C(CN)
CH ₂ O-N=C(Me)CH ₂ S	CH ₂ O-N=C(SMe)CH ₂ S	OCH ₂ CH ₂ O-N=C(Me)	C(Me)=N-O
O-N=CH	O-N=C(Me)	CH=N-N=C(Me)	C≡C
S(O)	CH ₂ SC(Et)=N	C≡C-C(=O)O	CH ₂ SC(c-Pr)=N

TABLE 7

Compounds of Formula I defined as:

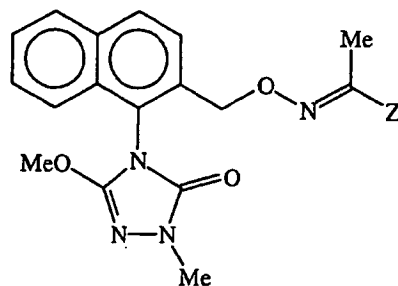


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph

(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienyloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 8

Compounds of Formula I defined as:

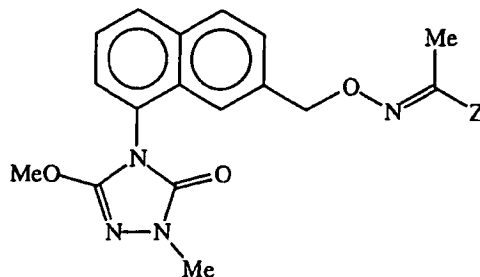


<u>Z</u>	<u>Z</u>	<u>Z</u>	<u>Z</u>
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl

2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
<i>c</i> -hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
3-CF ₃ -Ph	3-Et-Ph	2-pyrimidinyl	4-CF ₃ -2-pyridinyl
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph	3-Me ₃ Si-Ph	4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 9

Compounds of Formula I defined as:

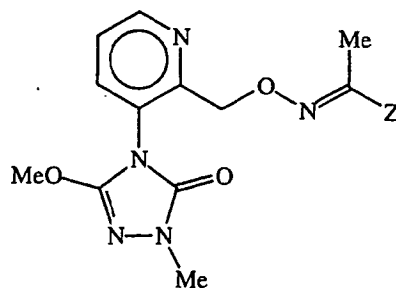


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
3-CF ₃ -Ph	3-Et-Ph	2-pyrimidinyl	4-CF ₃ -2-pyridinyl
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph	3-Me ₃ Si-Ph	4-OCF ₂ H-Ph	4-Ph-2-pyridinyl

<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 10

Compounds of Formula I defined as:

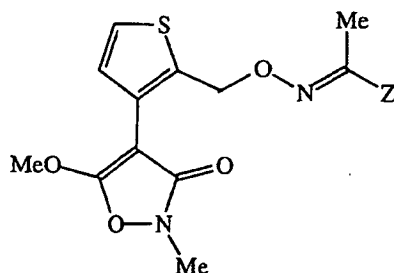


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
<i>c</i> -hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl

3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 11

Compounds of Formula I defined as:



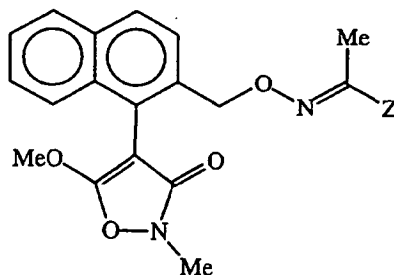
Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>r</i> -Bu-Ph	4- <i>r</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl

73

3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 12

Compounds of Formula I defined as:

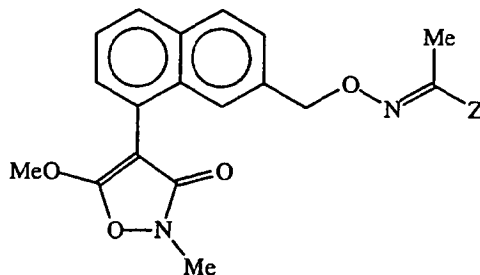


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
<i>c</i> -hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl

3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	4-CF ₃ -2-pyridinyl
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph	3-Me ₃ Si-Ph	4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 13

Compounds of Formula I defined as:

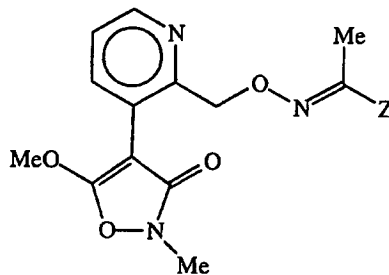


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
<i>c</i> -hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl

2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
3-CF ₃ -Ph	3-Et-Ph	2-pyrimidinyl	4-CF ₃ -2-pyridinyl
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph	3-Me ₃ Si-Ph	4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 14

Compounds of Formula I defined as:

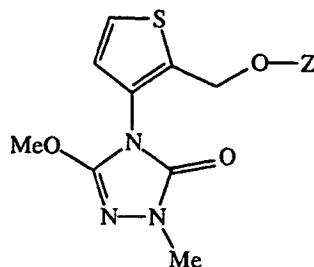


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph

4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinyloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinyloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienyloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 15

Compounds of Formula I defined as:

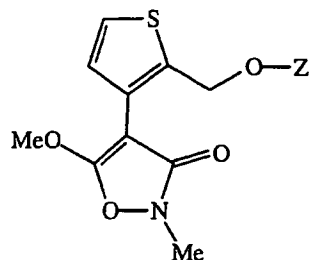


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl

2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl
4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 16

Compounds of Formula I defined as:

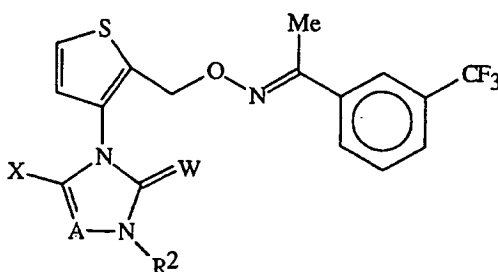


Z	Z	Z	Z
2-Br-Ph	PhCH=CHCH ₂	PhC≡CCH ₂	4-PhO-2-pyridinyl
2-CN-Ph	2-Me-Ph	2-Et-Ph	6-(2-CN-PhO)-4-pyrimidinyl
2,4-diCl-Ph	2-F-Ph	2-Cl-Ph	6-PhO-4-pyrimidinyl
2-CF ₃ -Ph	2-Me-4-Cl-Ph	2,4,6-triCl-Ph	4-EtO-2-pyrimidinyl
2-I-Ph	4-Ph-Ph	3-PhO-Ph	3-(4-pyrimidinylloxy)-Ph
c-hexyl	3-(2-Cl-PhO)-Ph	3-(2-Et-PhO)-Ph	4-(2-thienyl)Ph
4-NO ₂ -Ph	3,5-diCl-Ph	6-Ph-2-pyridinyl	3-(2-pyridinylloxy)Ph
PhCH ₂ CH ₂	3,5-diCF ₃ -Ph	6-PhO-4-pyridinyl	4-(3-Cl-2-pyridinylloxy)-Ph
(2-CN-Ph)CH ₂	2-MeO-Ph	3-thienylloxy-Ph	5-PhO-2-pyrimidinyl
CF ₃ CH ₂	2,6-diMeO-Ph	3-(4-CF ₃ -PhO)-Ph	6-(2-NO ₂ -PhO)-4-pyrimidinyl
2-MeS-Ph	3-(2-CN-PhO)-Ph	3-(2-Me-PhO)-Ph	6-(2-Cl-PhO)-4-pyrimidinyl
2-CF ₃ O-Ph	5-PhO-3-pyridinyl	5-PhO-2-pyridinyl	6-(2-CF ₃ -PhO)-4-pyrimidinyl
4-Me-Ph	6-Me-2-pyridinyl	6-PhO-2-pyridinyl	4,6-diMeO-2-pyrimidinyl
4-Cl-Ph	3-CF ₃ O-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
3-Me-Ph	4-Br-Ph	6-PhO-3-pyridinyl	6-CF ₃ -4-pyrimidinyl
	3-Et-Ph	2-pyrimidinyl	
3-Cl-2-Me-Ph	4-MeO-Ph	4-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
3- <i>t</i> -Bu-Ph	4- <i>t</i> -Bu-Ph	4-MeO-2-pyrimidinyl	6-CF ₃ -2-pyrazinyl
3-F-Ph	4-CN-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-CF ₃ -Ph	4-NO ₂ -Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
3,4-diCl-Ph	4-F-Ph	2-Ph-4-thiazolyl	5-CN-2-pyridinyl
3,4-diCF ₃ -Ph	3-Ph-Ph	3-MeO-6-pyridazinyl	6-Me-2-pyridinyl
3-EtO-Ph	3,4-diMe-Ph	5-Me-2-furanyl	4- <i>t</i> -Bu-2-nap
Ph	3,5-diMe-Ph	2,5-diMe-3-thienyl	3,5-diBr-Ph
2-nap	3-MeS-Ph	3-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3-SF ₅ -Ph		4-OCF ₂ H-Ph	4-Ph-2-pyridinyl
<i>t</i> -Bu	4-Me ₃ Si-Ph	5-Me-2-nap	4-Me ₃ Si-2-pyridinyl

4-F-3-CF ₃ -Ph	3-Me ₃ Ge-Ph	6-Me ₃ Si-2-nap	4-Me ₃ Ge-2-pyridinyl
5-F-3-CF ₃ -Ph	4-Me ₃ Ge-Ph	7-OCF ₃ -2-nap	4-CF ₃ -2-nap

TABLE 17

Compounds of Formula I defined as:

5 $R^2 = \text{Me}, W = O$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
		MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -Pr)O	N	(<i>c</i> -Pr)S	N	(<i>c</i> -Pr)O	CH	(<i>c</i> -Pr)S	CH

 $R^2 = \text{Et}, W = O$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -Pr)O	N	(<i>c</i> -Pr)S	N	(<i>c</i> -Pr)O	CH	(<i>c</i> -Pr)S	CH

 $R^2 = \text{Me}, W = S$

\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}	\underline{X}	\underline{A}
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH

80

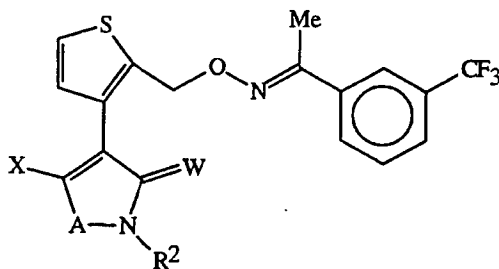
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -Pr)O	N	(<i>c</i> -Pr)S	N	(<i>c</i> -Pr)O	CH	(<i>c</i> -Pr)S	CH

 $R^2 = Et, W = S$

<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>
MeO	N	MeS	N	MeO	CH	MeS	CH
EtO	N	EtS	N	EtO	CH	EtS	CH
<i>n</i> -PrO	N	<i>n</i> -PrS	N	<i>n</i> -PrO	CH	<i>n</i> -PrS	CH
H ₂ C=CHCH ₂ O	N	H ₂ C=CHCH ₂ S	N	H ₂ C=CHCH ₂ O	CH	H ₂ C=CHCH ₂ S	CH
HC≡CCH ₂ O	N	HC≡CCH ₂ S	N	HC≡CCH ₂ O	CH	HC≡CCH ₂ S	CH
CF ₃ O	N	CF ₃ S	N	CF ₃ O	CH	CF ₃ S	CH
(<i>c</i> -Pr)O	N	(<i>c</i> -Pr)S	N	(<i>c</i> -Pr)O	CH	(<i>c</i> -Pr)S	CH

TABLE 18

Compounds of Formula I defined as:



5

 $R^2 = Me, W = O$

<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>
EtO	O	EtS	O	MeO	S	MeS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	EtO	S	EtS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
(<i>c</i> -Pr)O	O	(<i>c</i> -Pr)S	O	CF ₃ O	S	CF ₃ S	S
				(<i>c</i> -Pr)O	S	(<i>c</i> -Pr)S	S

$R^2 = Et, W = O$

<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -Pr)O	O	(<i>c</i> -Pr)S	O	(<i>c</i> -Pr)O	S	(<i>c</i> -Pr)S	S

 $R^2 = Me, W = S$

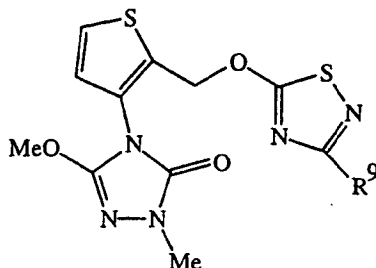
<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -Pr)O	O	(<i>c</i> -Pr)S	O	(<i>c</i> -Pr)O	S	(<i>c</i> -Pr)S	S

 $R^2 = Et, W = S$

<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>	<u>X</u>	<u>A</u>
MeO	O	MeS	O	MeO	S	MeS	S
EtO	O	EtS	O	EtO	S	EtS	S
<i>n</i> -PrO	O	<i>n</i> -PrS	O	<i>n</i> -PrO	S	<i>n</i> -PrS	S
H ₂ C=CHCH ₂ O	O	H ₂ C=CHCH ₂ S	O	H ₂ C=CHCH ₂ O	S	H ₂ C=CHCH ₂ S	S
HC≡CCH ₂ O	O	HC≡CCH ₂ S	O	HC≡CCH ₂ O	S	HC≡CCH ₂ S	S
CF ₃ O	O	CF ₃ S	O	CF ₃ O	S	CF ₃ S	S
(<i>c</i> -Pr)O	O	(<i>c</i> -Pr)S	O	(<i>c</i> -Pr)O	S	(<i>c</i> -Pr)S	S

TABLE 19

Compounds of Formula I defined as:



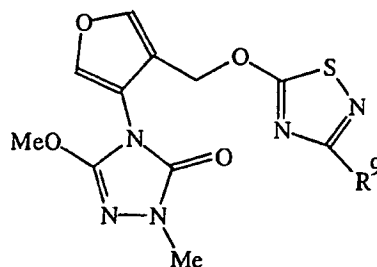
R ⁹	R ⁹	R ⁹	R ⁹
2-Br-Ph	2-Me-Ph	2-Et-Ph	4-EtO-2-pyrimidinyl
2-CN-Ph	2-F-Ph	2-Cl-Ph	4,6-diMeO-2-pyrimidinyl
2,4-diCl-Ph	2-Me-4-Cl-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
2-CF ₃ -Ph	3,5-diCl-Ph	2-pyrimidinyl	6-CF ₃ -4-pyrimidinyl
2-I-Ph	3,5-diCF ₃ -Ph	4-pyrimidinyl	4-CF ₃ -2-pyridinyl
4-NO ₂ -Ph	2-MeO-Ph	4-MeO-2-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
4-CF ₃ O-Ph	2,6-diMeO-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-Me-Ph	3-CF ₃ O-Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
4-Cl-Ph	4-Br-Ph	5-Me-2-furanyl	5-CN-2-pyridinyl
3-Me-Ph	3-Et-Ph	2,5-diMe-3-thienyl	6-Me-2-pyridinyl
3-CF ₃ -Ph	4-MeO-Ph	3-OCF ₂ H-Ph	3,5-diBr-Ph
3-Cl-2-Me-Ph	4- <i>t</i> -Bu-Ph	4-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3- <i>t</i> -Bu-Ph	4-CN-Ph	3-Me ₃ Si-Ph	4-Me ₃ Si-2-pyridinyl
3-F-Ph	4-NO ₂ -Ph	4-Me ₃ Si-Ph	4-Me ₃ Ge-2-pyridinyl
4-CF ₃ -Ph	3,4-diMe-Ph	3-Me ₃ Ge-Ph	4,6-diCF ₃ -2-pyrimidinyl
3,4-diCl-Ph	3,5-diMe-Ph	4-Me ₃ Ge-Ph	5-CF ₃ -2-furanyl
3,4-diCF ₃ -Ph	4-F-3-CF ₃ -Ph	3-EtO-Ph	5-CF ₃ -2-thienyl
4-F-Ph	5-F-3-CF ₃ -Ph	Ph	(2-CN-Ph)CH ₂
3,4-diF-Ph	3-Br-4-MeO-Ph	4,5-diBr-2-thienyl	(2-CF ₃ -Ph)CH ₂
3-Cl-4-Me-Ph	5-F-2-thienyl	4,5-diCl-2-thienyl	(3-CF ₃ -Ph)CH ₂
3,5-diF-Ph	5-Br-2-thienyl	4,5-diF-2-thienyl	(4-CF ₃ -Ph)CH ₂
3-F-4-Cl-Ph	5-Cl-2-thienyl	2-CF ₃ CH ₂ O-5-pyridinyl	(3,5-diCF ₃ -Ph)CH ₂
3-MeO-Ph	2,5-diF-3-thienyl	(4-Cl-Ph)CH ₂	(2-CF ₃ O-Ph)CH ₂
3-Cl-Ph	2,5-diCl-3-thienyl	(3-Cl-Ph)CH ₂	(3-CF ₃ O-Ph)CH ₂
<i>t</i> -Bu	2,5-diBr-3-thienyl	(2-Cl-Ph)CH ₂	(4-CF ₃ O-Ph)CH ₂

83

3-Br-Ph	2-I-Ph	(2-Br-Ph)CH ₂	2,6-diCl-4-pyridinyl
4-Ph-Ph	3-I-Ph	(3-Br-Ph)CH ₂	(2,6-diCl-Ph)CH ₂
4-Br-3-Me-Ph	2-Br-5-pyridinyl	(4-Br-Ph)CH ₂	

TABLE 20

Compounds of Formula I defined as:



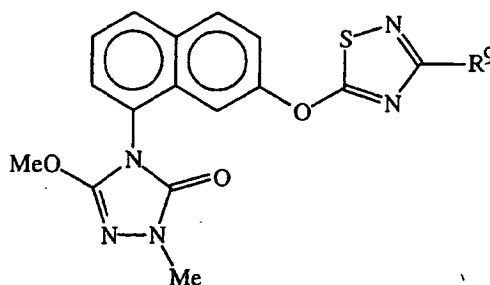
5

R ⁹	R ⁹	R ⁹	R ⁹
2-Br-Ph	2-Me-Ph	2-Et-Ph	4-EtO-2-pyrimidinyl
2-CN-Ph	2-F-Ph	2-Cl-Ph	4,6-diMeO-2-pyrimidinyl
2,4-diCl-Ph	2-Me-4-Cl-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
2-CF ₃ -Ph	3,5-diCl-Ph	2-pyrimidinyl	6-CF ₃ -4-pyrimidinyl
2-I-Ph	3,5-diCF ₃ -Ph	4-pyrimidinyl	4-CF ₃ -2-pyridinyl
4-NO ₂ -Ph	2-MeO-Ph	4-MeO-2-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
4-CF ₃ O-Ph	2,6-diMeO-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-Me-Ph	3-CF ₃ O-Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
4-Cl-Ph	4-Br-Ph	5-Me-2-furanyl	5-CN-2-pyridinyl
3-Me-Ph	3-Et-Ph	2,5-diMe-3-thienyl	6-Me-2-pyridinyl
3-CF ₃ -Ph	4-MeO-Ph	3-OCF ₂ H-Ph	3,5-diBr-Ph
3-Cl-2-Me-Ph	4- <i>t</i> -Bu-Ph	4-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3- <i>t</i> -Bu-Ph	4-CN-Ph	3-Me ₃ Si-Ph	4-Me ₃ Si-2-pyridinyl
3-F-Ph	4-NO ₂ -Ph	4-Me ₃ Si-Ph	4-Me ₃ Ge-2-pyridinyl
4-CF ₃ -Ph	3,4-diMe-Ph	3-Me ₃ Ge-Ph	4,6-diCF ₃ -2-pyrimidinyl
3,4-diCl-Ph	3,5-diMe-Ph	4-Me ₃ Ge-Ph	5-CF ₃ -2-furanyl
3,4-diCF ₃ -Ph	4-F-3-CF ₃ -Ph	3-EtO-Ph	5-CF ₃ -2-thienyl
4-F-Ph	5-F-3-CF ₃ -Ph	Ph	(2-CN-Ph)CH ₂
3,4-diF-Ph	3-Br-4-MeO-Ph	4,5-diBr-2-thienyl	(2-CF ₃ -Ph)CH ₂
3-Cl-4-Me-Ph	5-F-2-thienyl	4,5-diCl-2-thienyl	(3-CF ₃ -Ph)CH ₂
3,5-diF-Ph	5-Br-2-thienyl	4,5-diF-2-thienyl	(4-CF ₃ -Ph)CH ₂

3-F-4-Cl-Ph	5-Cl-2-thienyl	2-CF ₃ CH ₂ O-5-pyridinyl	(3,5-diCF ₃ -Ph)CH ₂
3-MeO-Ph	2,5-diF-3-thienyl	(4-Cl-Ph)CH ₂	(2-CF ₃ O-Ph)CH ₂
3-Cl-Ph	2,5-diCl-3-thienyl	(3-Cl-Ph)CH ₂	(3-CF ₃ O-Ph)CH ₂
<i>t</i> -Bu	2,5-diBr-3-thienyl	(2-Cl-Ph)CH ₂	(4-CF ₃ O-Ph)CH ₂
3-Br-Ph	2-I-Ph	(2-Br-Ph)CH ₂	2,6-diCl-4-pyridinyl
4-Ph-Ph	3-I-Ph	(3-Br-Ph)CH ₂	(2,6-diCl-Ph)CH ₂
4-Br-3-Me-Ph	2-Br-5-pyridinyl	(4-Br-Ph)CH ₂	

TABLE 21

Compounds of Formula I defined as:



5

R ⁹	R ⁹	R ⁹	R ⁹
2-Br-Ph	2-Me-Ph	2-Et-Ph	4-EtO-2-pyrimidinyl
2-CN-Ph	2-F-Ph	2-Cl-Ph	4,6-diMeO-2-pyrimidinyl
2,4-diCl-Ph	2-Me-4-Cl-Ph	6-CF ₃ -2-pyridinyl	4,6-diMe-2-pyrimidinyl
2-CF ₃ -Ph	3,5-diCl-Ph	2-pyrimidinyl	6-CF ₃ -4-pyrimidinyl
2-I-Ph	3,5-diCF ₃ -Ph	4-pyrimidinyl	4-CF ₃ -2-pyridinyl
4-NO ₂ -Ph	2-MeO-Ph	4-MeO-2-pyrimidinyl	4-CF ₃ -2-pyrimidinyl
4-CF ₃ O-Ph	2,6-diMeO-Ph	4-Me-2-pyrimidinyl	5-CF ₃ -3-pyridinyl
4-Me-Ph	3-CF ₃ O-Ph	6-MeO-4-pyrimidinyl	3-MeO-2-pyridinyl
4-Cl-Ph	4-Br-Ph	5-Me-2-furanyl	5-CN-2-pyridinyl
3-Me-Ph	3-Et-Ph	2,5-diMe-3-thienyl	6-Me-2-pyridinyl
3-CF ₃ -Ph	4-MeO-Ph	3-OCF ₂ H-Ph	3,5-diBr-Ph
3-Cl-2-Me-Ph	4- <i>t</i> -Bu-Ph	4-OCF ₂ H-Ph	4- <i>t</i> -Bu-2-pyridinyl
3- <i>t</i> -Bu-Ph	4-CN-Ph	3-Me ₃ Si-Ph	4-Me ₃ Si-2-pyridinyl
3-F-Ph	4-NO ₂ -Ph	4-Me ₃ Si-Ph	4-Me ₃ Ge-2-pyridinyl
4-CF ₃ -Ph	3,4-diMe-Ph	3-Me ₃ Ge-Ph	4,6-diCF ₃ -2-pyrimidinyl
3,4-diCl-Ph	3,5-diMe-Ph	4-Me ₃ Ge-Ph	5-CF ₃ -2-furanyl
3,4-diCF ₃ -Ph	4-F-3-CF ₃ -Ph	3-EtO-Ph	5-CF ₃ -2-thienyl

4-F-Ph	5-F-3-CF ₃ -Ph	Ph	(2-CN-Ph)CH ₂
3,4-diF-Ph	3-Br-4-MeO-Ph	4,5-diBr-2-thienyl	(2-CF ₃ -Ph)CH ₂
3-Cl-4-Me-Ph	5-F-2-thienyl	4,5-diCl-2-thienyl	(3-CF ₃ -Ph)CH ₂
3,5-diF-Ph	5-Br-2-thienyl	4,5-diF-2-thienyl	(4-CF ₃ -Ph)CH ₂
3-F-4-Cl-Ph	5-Cl-2-thienyl	2-CF ₃ CH ₂ O-5-pyridinyl	(3,5-diCF ₃ -Ph)CH ₂
3-MeO-Ph	2,5-diF-3-thienyl	(4-Cl-Ph)CH ₂	(2-CF ₃ O-Ph)CH ₂
3-Cl-Ph	2,5-diCl-3-thienyl	(3-Cl-Ph)CH ₂	(3-CF ₃ O-Ph)CH ₂
<i>t</i> -Bu	2,5-diBr-3-thienyl	(2-Cl-Ph)CH ₂	(4-CF ₃ O-Ph)CH ₂
3-Br-Ph	2-I-Ph	(2-Br-Ph)CH ₂	2,6-diCl-4-pyridinyl
4-Ph-Ph	3-I-Ph	(3-Br-Ph)CH ₂	(2,6-diCl-Ph)CH ₂
4-Br-3-Me-Ph	2-Br-5-pyridinyl	(4-Br-Ph)CH ₂	

Formulation/Utility

Compounds of this invention will generally be used as a formulation or composition with an agriculturally suitable carrier comprising at least one of a liquid diluent, a solid diluent or a surfactant. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5-90	0-94	1-15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp.,
 5 Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated
 10 alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar,
 15 silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkyl naphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty
 20 acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as
 25 in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling;

see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Tables A-G.

Example A

Wettable Powder

Compound 17	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%

Example B

Granule

Compound 17	10.0%
attapulgate granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%

Example CExtruded Pellet

	Compound 17	25.0%
	anhydrous sodium sulfate	10.0%
5	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%

Example DEmulsifiable Concentrate

10	Compound 17	20.0%
	blend of oil soluble sulfonates	
	and polyoxyethylene ethers	10.0%
	isophorone	70.0%

- The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and Deuteromycete classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*, *Alternaria brassicae*, *Septoria nodorum*, *Septoria tritici*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercospora herpotrichoides*, *Cercospora beticola*, *Botrytis cinerea*, *Monilinia fructicola*, *Pyricularia oryzae*, *Podosphaera leucotricha*, *Venturia inaequalis*, *Erysiphe graminis*, *Uncinula necator*, *Puccinia recondita*, *Puccinia graminis*, *Hemileia vastatrix*, *Puccinia striiformis*, *Puccinia arachidis*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, *Fusarium oxysporum*, *Verticillium dahliae*, *Pythium aphanidermatum*, *Phytophthora megasperma*, *Sclerotinia sclerotiorum*, *Sclerotium rolfsii*, *Erysiphe polygoni*, *Pyrenophora teres*, *Gaeumannomyces graminis*, *Rhynchosporium secalis*, *Fusarium roseum*, *Bremia lactucae* and other genera and species closely related to these pathogens.
- Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators,

chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such agricultural protectants with which compounds of this invention can be formulated are: insecticides

5 such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor,

10 monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflumuron; fungicides such as azoxystrobin (ICIA5504), benomyl, blasticidin-S, Bordeaux mixture (tribasic copper sulfate), bromuconazole, captafol, captan,

15 carbendazim, chloroneb, chlorothalonil, copper oxychloride, copper salts, cymoxanil, cyproconazole, cyprodinil (CGA 219417), diclomezine, dicloran, difenoconazole, dimethomorph, diniconazole, diniconazole-M, dodine, edifenphos, epoxyconazole (BAS 480F), fenarimol, fenbuconazole, fenciclonil, fenpropidin, fenpropimorph, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fosetyl-aluminum, furalaxyl,

20 hexaconazole, ipconazole, iprobenfos, iprodione, isoprothiolane, kasugamycin, kresoxim-methyl (BAS 490F), mancozeb, maneb, mepronil, metalaxyl, metconazole, myclobutanil, neo-asozin (ferric methanearsonate), oxadixyl, penconazole, pencycuron, probenazole, prochloraz, propiconazole, pyrifenoxy, pyroquilon, sulfur, tebuconazole, tetraconazole, thiabendazole, thiophanate-methyl, thiram, triadimefon, triadimenol,

25 tricyclazole, triticonazole, uniconazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis*

30 delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.

In certain instances, combinations with other fungicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Preferred for better control of plant diseases caused by fungal plant pathogens

35 (e.g., lower use rate or broader spectrum of plant pathogens controlled) or resistance management are mixtures of a compound of this invention with a fungicide selected from

the group cyproconazole, cyprodinil (CGA 219417), epoxyconazole (BAS 480F), fenpropidin, fenpropimorph, flusilazole and tebuconazole. Specifically preferred mixtures (compound numbers refer to compounds in Index Tables A-G) are selected from the group: compound 1 and cyproconazole; compound 1 and cyprodinil
5 (CGA 219417); compound 1 and epoxyconazole (BAS 480F); compound 1 and fenpropidin; compound 1 and fenpropimorph; compound 1 and flusilazole; compound 1 and tebuconazole; compound 2 and cyproconazole; compound 2 and cyprodinil (CGA 219417); compound 2 and epoxyconazole (BAS 480F); compound 2 and fenpropidin; compound 2 and fenpropimorph; compound 2 and flusilazole; compound 2
10 and tebuconazole; compound 4 and cyproconazole; compound 4 and cyprodinil (CGA 219417); compound 4 and epoxyconazole (BAS 480F); compound 4 and fenpropidin; compound 4 and fenpropimorph; compound 4 and flusilazole; compound 4 and tebuconazole; compound 6 and cyproconazole; compound 6 and cyprodinil (CGA 219417); compound 6 and epoxyconazole (BAS 480F); compound 6 and
15 fenpropidin; compound 6 and fenpropimorph; compound 6 and flusilazole; compound 6 and tebuconazole; compound 15 and cyproconazole; compound 15 and cyprodinil (CGA 219417); compound 15 and epoxyconazole (BAS 480F); compound 15 and fenpropidin; compound 15 and fenpropimorph; compound 15 and flusilazole; compound 15 and tebuconazole; compound 17 and cyproconazole; compound 17 and
20 cyprodinil (CGA 219417); compound 17 and epoxyconazole (BAS 480F); compound 17 and fenpropidin; compound 17 and fenpropimorph; compound 17 and flusilazole; and compound 15 and tebuconazole.

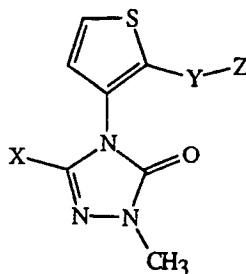
Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant to
25 be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed to protect the seed and seedling.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can
30 normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of active ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g per kilogram of seed.

The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the
35 compounds is not limited, however, to these species. See Index Tables A-G for compound descriptions. The following abbreviations are used in the Index Tables which

follow: Ph = phenyl and PhO = phenoxy. The abbreviation "Ex." stands for "Example" and is followed by a number indicating in which example the compound is prepared.

INDEX TABLE A



5

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
1 Ex. 2	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-(CH ₃) ₃ Si-Ph	oil/gum*
2 Ex. 3	CH ₃ O	-CH ₂ O-	2,5-diCH ₃ -Ph	151-153
3 Ex. 1	CH ₃ O	direct bond	CH ₂ Br	117-118
4	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-CF ₃ -Ph	91-93
5 ^a Ex. 4	CH ₃ O	-CH=C(Cl)-C(=O)-O-	<i>t</i> -Bu	105-115
6 ^b Ex. 4	CH ₃ O	-CH=C(Cl)-C(=O)-O-	<i>t</i> -Bu	104
7	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	4-CF ₃ -pyridin-2-yl	101-103.5
8	CH ₃ O	direct bond	3-(3-CF ₃ -Ph)-1,2,4-oxadiazol-5-yl	158
9	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,4-diCl-Ph	132-134
10	CH ₃ O	-CH ₂ O-N=C(NH ₂)-	3-CF ₃ -Ph	123-124
11	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,5-diBr-Ph	150.5-151
12	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,5-diCl-Ph	159-160
13	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	2-naphthalenyl	124-125
14 ^c	CH ₃ O	-CH ₂ O-N=C(CH ₂ CH ₃)-	3-CF ₃ -Ph	oil*
15	CH ₃ O	-CH ₂ O-	3-(4-Cl-Ph)-1,2,4-thiadiazol-5-yl	184-185
16	CH ₃ O	-CH ₂ O-	3-(3,5-diCl-Ph)-1,2,4-thiadiazol-5-yl	185-186
17 Ex. 10	CH ₃ O	-CH ₂ O-	3-(4-CF ₃ -Ph)-1,2,4-thiadiazol-5-yl	138-139

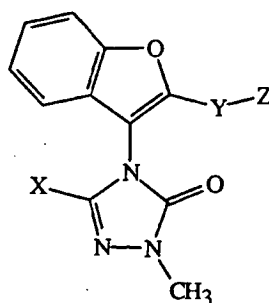
*See Index Table G for ¹H NMR data.

^aCompound isolated in a 7:3 ratio of *Z* and *E* isomers, respectively.

10 ^bCompound isolated in a 5:1 ratio of *Z* and *E* isomers, respectively.

*Compound contains 28% by weight of 2,4-dihydro-5-methoxy-2-methyl-4-[5-methyl-2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3H-1,2,4-triazol-3-one which is also a compound of this invention.

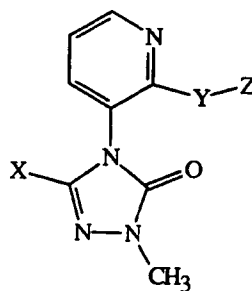
5

INDEX TABLE B

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
18	CH ₃ O	direct bond	CH ₂ Br	132-133
19	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,4-diCl-Ph	143-144
20	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-(CH ₃) ₃ Si-Ph	oil*
21	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	4-CF ₃ -pyridin-2-yl	123-125
22	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-CF ₃ -Ph	87-89

*See Index Table G for ¹H NMR data.

10

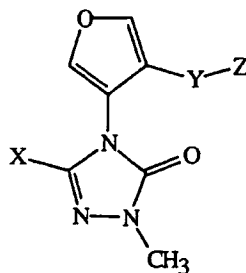
INDEX TABLE C

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
23	Cl	direct bond	CH ₃	99-101
24	CH ₃ O	direct bond	CH ₃	123-125
25	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-CF ₃ -Ph	oil*

26	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	4-CF ₃ -pyridin-2-yl	106-107
27	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,4-diCl-Ph	102-104
28	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-(CH ₃) ₃ Si-Ph	135-137
29	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,5-diCl-Ph	135-137
30	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,5-diBr-Ph	145-147
31	CH ₃ O	-CH ₂ O-N=C(NH ₂)-	3-CF ₃ -Ph	147-148
32	CH ₃ O	-CH ₂ S-	5-CF ₃ -4 <i>H</i> -1,2,4-triazol-3-yl	178-179
33	CH ₃ O	direct bond	3-(3-CF ₃ -Ph)-1,2,4-oxadiazol-5-yl	165-166
34	CH ₃ O	-CH ₂ -	3-CF ₃ -1 <i>H</i> -pyrazol-1-yl	99-100
35	CH ₃ O	-CH ₂ O-	2-Cl-5-CF ₃ -Ph	106-108
36	CH ₃ O	-CH ₂ O-	2,5-diCH ₃ -Ph	91-93
37	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	2-naphthalenyl	semisolid*
38 Ex. 9	CH ₃ O	-O-	3-PhO-Ph	113-114
39 Ex. 8	Cl	-O-	3-PhO-Ph	72-75

*See Index Table G for ¹H NMR data.

INDEX TABLE D



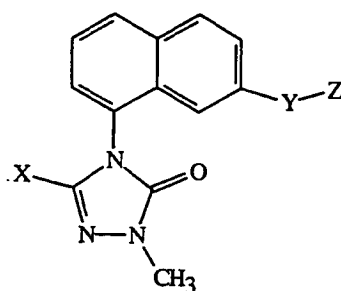
5

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
40	CH ₃ O	direct bond	3-(3-CF ₃ -Ph)-1,2,4-oxadiazol-5-yl	149-150
41 Ex. 5	CH ₃ O	direct bond	CH ₂ Br	147-149
42	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	2-naphthalenyl	134-136
43	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,4-diCl-Ph	118-119
44	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	4-CF ₃ -pyridin-2-yl	125-127
45	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3,5-diCl-Ph	148.5-150.5
46 Ex. 6	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-(CH ₃) ₃ Si-Ph	oil*
47	CH ₃ O	-CH ₂ O-N=C(NH ₂)-	3-CF ₃ -Ph	semisolid*
48	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-CF ₃ -Ph	81-83

49 CH₃O -CH₂O-N=C(CH₃)- 3,5-diBr-Ph 126.5-127.5

*See Index Table G for ¹H NMR data.

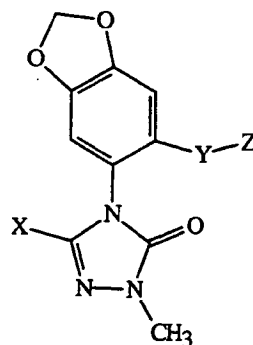
INDEX TABLE E



5

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
50 Ex. 7	CH ₃ O	-O-	3-(4-CF ₃ -Ph)-1,2,4-thiadiazol-5-yl	216-217
51	CH ₃ O	-O-	3-(3,5-diCl-Ph)-1,2,4-thiadiazol-5-yl	222-223
52	CH ₃ O	-O-	3-(4-Cl-Ph)-1,2,4-thiadiazol-5-yl	226-227

INDEX TABLE F



10

<u>Cmpd No.</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>m.p. (°C)</u>
53	CH ₃ O	-CH ₂ O-N=C(CH ₃)-	3-CF ₃ -Ph	153-155

INDEX TABLE G

<u>Cmpd No.</u>	<u>¹H NMR Data (CDCl₃ solution unless indicated otherwise)^a</u>
1	δ 7.76 (s,1H), 7.60 (m,1H), 7.54 (m,1H), 7.36 (d,1H), 7.32 (d,1H), 6.94 (d,1H), 5.29 (s,2H), 3.89 (s,3H), 3.41 (s,3H), 2.21 (s,3H), 0.28 (s,9H).

- 14 major component: δ 7.33 (d,1H), 6.95 (d,1H), 5.31 (d,2H), 3.904 (s,3H), 3.42 (s,3H), 2.74 (q,2H), 1.11 (t,3H) plus peaks overlapping with minor component at 7.88 (d), 7.79 (m), 7.61 (d), 7.49 (t);
minor component: δ 6.62 (s,1H), 5.22 (d,2H), 3.899 (s,3H), 3.41 (s,3H), 2.45 (s,3H), 2.22 (d,3H) plus peaks overlapping with major component at 7.88 (d), 7.79 (m), 7.61 (d), 7.49 (t).
- 20 δ 7.67 (s,1H), 7.52 (m,3H), 7.40 (d,1H), 7.33 (m,2H), 7.26 (m,1H), 5.35 (br s,2H), 3.77 (s,3H), 3.44 (s,3H), 2.20 (s,3H), 0.27 (s,9H).
- 25 δ 8.68 (m,1H), 7.80 (s,1H), 7.75 (d,1H), 7.60 (m,2H), 7.47-7.37 (m,2H), 5.47 (AB pattern, 2H), 3.82 (s,3H), 3.35 (s,3H), 2.16 (s,3H).
- 37 δ 8.69 (m,1H), 7.94 (s,1H), 7.85-7.73 (m,4H), 7.61 (d,1H), 7.59-7.45 (m,2H), 7.38 (dd,1H), 5.50 (AB pattern, 2H), 3.78 (s,3H); 3.35 (s,3H), 2.25 (s,3H).
- 46 δ 7.70 (s,1H), 7.54 (m,4H), 7.34 (t,1H), 5.11 (s,2H), 3.86 (s,3H), 3.32 (s,3H), 2.14 (s,3H), 0.28 (s,9H).
- 47 δ 7.86 (s,1H), 7.76 (d,1H), 7.64 (d,1H), 7.59 (d,1H), 7.54 (d,1H), 7.53-7.47 (m,1H), 5.01 (br s,2H), 4.96 (s,2H), 3.89 (s,3H), 3.33 (s,3H).

^a ¹H NMR data are in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet, (dd)-doublet of doublets, (br s)-broad singlet.

5

BIOLOGICAL EXAMPLES OF THE INVENTION

Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem[®] 014 (polyhydric alcohol esters). The resulting test suspensions were then used in the following tests. Spraying these 200 ppm test suspensions to the point of run-off on the test plants is the equivalent of a rate of 500 g/ha.

10

TEST A

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

15

TEST B

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

TEST C

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h, and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

TEST D

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

TEST E

The test suspension was sprayed to the point of run-off on grape seedlings. The following day the seedlings were inoculated with a spore suspension of *Plasmopara viticola* (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C for 24 h, after which disease ratings were made.

TEST F

The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of *Botrytis cinerea* (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A dash (-) indicates no test results.

Table A

<u>Cmpd No.</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>	<u>Test F</u>
1	100	100	94	0	16*	41
2	100	93	0	24	0*	41
3	46	0	0	0	13*	0
4	100	100	97	0	17*	66
5	97	100	0	-	0*	0
6	97	100	52	0	17*	41
7	97	100	86	0	8*	42
8	99	97	74	10	21*	0
9	91	99	53	86	49*	0
10	82	97	32	72	6**	0
11	100	99	53	91	100**	82
12	100	100	53	39	95*	43
13	100	100	91	73	88*	67
14	100	100	85	56	28*	82
15	94	99	26	0	42*	82
16	99	97	26	0	40*	90
17	98	99	90	0	48*	69
18	53	61	0	0	30*	0
19	91	0	0	22	0*	0
20	59	84	0	0	8*	0
21	31	93	0	0	29*	0
22	91	66	0	0	0*	0
23	0	0	0	0	3*	0
24	0	0	0	0	3*	0
25	98	97	0	0	22*	46
26	99	100	0	0	2*	10
27	76	99	0	0	2*	0
28	100	100	32	0	14*	90
29	100	100	53	0	23*	48
30	99	99	53	0	7*	70
31	60	0	0	0	7*	68
32	0	0	0	0	7*	44
33	97	85	0	46	6*	0

98

34	0	66	0	25	13*	57
35	36	66	0	11	7*	0
36	84	85	0	25	9*	0
37	25	93	53	25	0*	0
38	91	99	60	95	71*	77
39	61	86	74	0	-	0
40	61	85	0	26	2*	44
41	0	65	0	0	-	0
42	55	100	53	25	1*	5
43	100	99	32	-	11*	68
44	100	100	32	10	1*	94
45	100	99	53	72	1*	94
46	99	100	32	24	19*	46
47	0	0	0	0	37*	0
48	98	99	32	26	15*	41
49	99	94	53	72	12*	7
50	94	67	0	63	5*	94
51	85	0	0	16	-	0
52	85	26	0	42	-	0
53	57	86	0	0	5*	0

*Compound was tested at 10 ppm (equivalent to 25 g/ha).

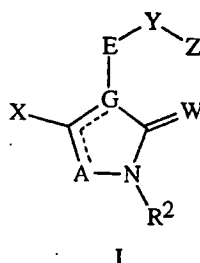
**Compound was tested at 40 ppm (equivalent to 100 g/ha).

CLAIMS

What is claimed is:

1. A compound selected from Formula I, *N*-oxides and agriculturally suitable salts thereof,

5



wherein

E is a ring system selected from:

10

- i) 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two Q as ring members and optionally includes one or two ring members independently selected from C(=O) and S(O)₂, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic heterocyclic ring system optionally substituted with one of R³, R⁴, or both R³ and R⁴; and

15

20

- ii) a naphthalene ring, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalene ring optionally substituted with one of R³, R⁴, or both R³ and R⁴, provided that when G is attached to the 1, 4, 5, or 8 position of the naphthalene ring and Z is C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl or phenyl each substituted with R⁹ and optionally substituted with one or more R¹⁰, then Y is other than -O-, -S(O)_n-, -C(=O)-, -CHR⁶-, -CHR⁶CHR⁶-, -CR⁶=CR⁶-, -C≡C-, -OCHR¹⁵-, -S(O)_nCHR¹⁵- or a direct bond;

25

A is O; S; N; NR⁵; or CR¹⁴;

G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR¹⁴ and the floating double bond is attached to A;

W is O; S; NH; N(C₁-C₆ alkyl); or NO(C₁-C₆ alkyl);

5 X is OR¹; S(O)_mR¹; or halogen;

R¹ is C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxycarbonyl;

10 R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxycarbonyl; hydroxy; C₁-C₂ alkoxy; or acetyloxy;

15 R³ and R⁴ are each independently halogen; cyano; nitro; hydroxy; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₂-C₆ alkenyloxy; C₂-C₆ alkynyloxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; formyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxycarbonyl; NH₂C(O); (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); Si(R²⁵)₃; Ge(R²⁵)₃; (R²⁵)₃Si-C≡C-; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R⁸ and optionally substituted with one or more R¹⁰;

20 R⁵ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; C₂-C₄ alkylcarbonyl; or C₂-C₄ alkoxycarbonyl;

25 Y is -O-; -S(O)_n-; -NR¹⁵-; -C(=O)-; -CH(OR¹⁵)-; -CHR⁶-; -CHR⁶CHR⁶-; -CR⁶=CR⁶-; -C≡C-; -CHR¹⁵O-; -OCHR¹⁵-; -CHR¹⁵S(O)_n-; -S(O)_nCHR¹⁵-; -CHR¹⁵O-N=C(R⁷)-; -(R⁷)C=N-OCHR¹⁵-; -C(R⁷)=N-O-; -O-N=C(R⁷)-; -CHR¹⁵OC(=O)N(R¹⁵)-; -CHR¹⁵OC(=S)N(R¹⁵)-; -CHR¹⁵OC(=O)O-; -CHR¹⁵OC(=S)O-; -CHR¹⁵OC(=O)S-; -CHR¹⁵OC(=S)S-; -CHR¹⁵SC(=O)N(R¹⁵)-; -CHR¹⁵SC(=S)N(R¹⁵)-; -CHR¹⁵SC(=O)O-; -CHR¹⁵SC(=S)O-; -CHR¹⁵SC(=O)S-; -CHR¹⁵SC(=S)S-; -CHR¹⁵SC(=NR¹⁵)S-; -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-; -CHR¹⁵O-N(R¹⁵)C(=O)N(R¹⁵)-; -CHR¹⁵O-N(R¹⁵)C(=S)N(R¹⁵)-; -CHR¹⁵O-N=C(R⁷)NR¹⁵-; -CHR¹⁵O-N=C(R⁷)OCH₂-; -CHR¹⁵O-N=C(R⁷)-N=N-; -CHR¹⁵O-N=C(R⁷)-C(=O)-; -CHR¹⁵O-N=C(R⁷)-C(=N-A²-Z¹)-A¹-; -CHR¹⁵O-N=C(R⁷)-C(R⁷)=N-A²-A³-; -CHR¹⁵O-N=C(C(R⁷)=N-A²-Z¹)-; -CHR¹⁵O-N=C(R⁷)-CH₂O-; -CHR¹⁵O-N=C(R⁷)-CH₂S-;

30

35

5
 -O-CH₂CH₂O-N=C(R⁷)-; -CHR¹⁵O-C(R¹⁵)=C(R⁷)-; -CHR¹⁵O-C(R⁷)=N-;
 -CHR¹⁵S-C(R⁷)=N-; -C(R⁷)=N-NR¹⁵-; -CH=N-N=C(R⁷)-;
 -CHR¹⁵N(R¹⁵)-N=C(R⁷)-; -CHR¹⁵N(COCH₃)-N=C(R⁷)-;
 -OC(=S)NR¹⁵C(=O)-; -CHR⁶-C(=W¹)-A¹-; -CHR⁶CHR⁶-C(=W¹)-A¹-;
 -CR⁶=CR⁶-C(=W¹)-A¹-; -C≡C-C(=W¹)-A¹-; -N=CR⁶-C(=W¹)-A¹-; or a
 direct bond; and the directionality of the Y linkage is defined such that the
 moiety depicted on the left side of the linkage is bonded to E and the moiety
 on the right side of the linkage is bonded to Z;

Z¹ is H or -A³-Z;

10 W¹ is O or S;

A¹ is O; S; NR¹⁵; or a direct bond;

A² is O; NR¹⁵; or a direct bond;

A³ is -C(=O)-; -S(O)₂-; or a direct bond;

15 each R⁶ is independently H; 1-2 CH₃; C₂-C₃ alkyl; C₁-C₃ alkoxy; C₃-C₆
 cycloalkyl; formylamino; C₂-C₄ alkylcarbonylamino; C₂-C₄
 alkoxycarbonylamino; NH₂C(O)NH; (C₁-C₃ alkyl)NHC(O)NH;
 (C₁-C₃ alkyl)₂NC(O)NH; N(C₁-C₃ alkyl)₂; piperidiny; morpholiny;
 1-2 halogen; cyano; or nitro;

20 each R⁷ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆
 haloalkoxy; C₁-C₆ alkylthio; C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; C₁-C₆
 haloalkylthio; C₁-C₆ haloalkylsulfinyl; C₁-C₆ haloalkylsulfonyl; C₂-C₆
 alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; C₃-C₆
 cycloalkyl; C₂-C₄ alkylcarbonyl; C₂-C₄ alkoxycarbonyl; halogen; cyano;
 nitro; hydroxy; amino; NH(C₁-C₆ alkyl); N(C₁-C₆ alkyl)₂; or morpholiny;

25 each Z is independently selected from:

- i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, and C₂-C₁₀ alkynyl each substituted with R⁹
 and optionally substituted with one or more R¹⁰;
- ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R⁹
 and optionally substituted with one or more R¹⁰;
- 30 iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic
 and fused tricyclic nonaromatic heterocyclic ring systems and 5 to
 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic
 heterocyclic ring systems, each heterocyclic ring system containing 1 to 6
 heteroatoms independently selected from the group nitrogen, oxygen, and
 35 sulfur, provided that each heterocyclic ring system contains no more than 4
 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each

nonaromatic or aromatic heterocyclic ring system substituted with R^9 and optionally substituted with one or more R^{10} ;

- iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing one or two nonaromatic rings that each include one or two Q as ring members and one or two ring members independently selected from $C(=O)$ and $S(O)_2$, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R^9 and optionally substituted with one or more R^{10} ; and
- v) adamantyl substituted with R^9 and optionally substituted with one or more R^{10} ;

each Q is independently selected from the group $-CHR^{13}$ -, $-NR^{13}$ -, $-O$ -, and $-S(O)_p$ -;

- R^8 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_1 - C_6 alkylthio; C_1 - C_6 haloalkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; C_3 - C_6 cycloalkyl; C_3 - C_6 alkenyloxy; $CO_2(C_1$ - C_6 alkyl); $NH(C_1$ - C_6 alkyl); $N(C_1$ - C_6 alkyl) $_2$; cyano; nitro; $SiR^{19}R^{20}R^{21}$; or $GeR^{19}R^{20}R^{21}$;

- R^9 is H; 1-2 halogen; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; C_2 - C_6 alkenyl; C_2 - C_6 haloalkenyl; C_2 - C_6 alkynyl; C_1 - C_6 alkylthio; C_1 - C_6 haloalkylthio; C_1 - C_6 alkylsulfinyl; C_1 - C_6 alkylsulfonyl; C_3 - C_6 cycloalkyl; C_3 - C_6 alkenyloxy; $CO_2(C_1$ - C_6 alkyl); $NH(C_1$ - C_6 alkyl); $N(C_1$ - C_6 alkyl) $_2$; $-C(R^{18})=NOR^{17}$; cyano; nitro; SF_5 ; $SiR^{22}R^{23}R^{24}$; or $GeR^{22}R^{23}R^{24}$; or R^9 is phenyl, benzyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl, or pyrimidinyloxy each optionally substituted with one of R^{11} , R^{12} , or both R^{11} and R^{12} ;

each R^{10} is independently halogen; C_1 - C_4 alkyl; C_1 - C_4 haloalkyl; C_1 - C_4 alkoxy; nitro; or cyano; or

- when R^9 and an R^{10} are attached to adjacent atoms on Z, R^9 and said adjacently attached R^{10} can be taken together as $-OCH_2O-$ or $-OCH_2CH_2O-$; each CH_2 group of said taken together R^9 and R^{10} optionally substituted with 1-2 halogen; or

when Y and an R^{10} are attached to adjacent atoms on Z and Y is

- $-CHR^{15}O-N=C(R^7)-$, $-O-N=C(R^7)-$, $-O-CH_2CH_2O-N=C(R^7)-$, $-CHR^{15}O-C(R^{15})=C(R^7)-$, $-CH=N-N=C(R^7)-$, $-CHR^{15}N(R^{15})-N=C(R^7)-$ or

- CHR¹⁵N(COCH₃)-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken together as -(CH₂)_r-J- such that J is attached to Z;
- J is -CH₂-; -CH₂CH₂-; -OCH₂-; -CH₂O-; -SCH₂-; -CH₂S-; -N(R¹⁶)CH₂-; or -CH₂N(R¹⁶)-; each CH₂ group of said J optionally substituted with 1 to 2 CH₃;
- R¹¹ and R¹² are each independently halogen; C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₁-C₄ alkoxy; C₁-C₄ haloalkoxy; nitro; cyano; Si(R²⁵)₃; or Ge(R²⁵)₃;
- each R¹³ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- R¹⁴ is H; halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl; or C₃-C₆ cycloalkyl;
- each R¹⁵ is independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; or
- when Y is -CHR¹⁵N(R¹⁵)C(=O)N(R¹⁵)-, the two R¹⁵ attached to nitrogen atoms on said group can be taken together as -(CH₂)_s-; or
- when Y is -CHR¹⁵O-N=C(R⁷)NR¹⁵-, R⁷ and the adjacently attached R¹⁵ can be taken together as -CH₂-(CH₂)_s-; -O-(CH₂)_s-; -S-(CH₂)_s-; or -N(C₁-C₃ alkyl)-(CH₂)_s-; with the directionality of said linkage defined such that the moiety depicted on the left side of the linkage is bonded to the carbon and the moiety on the right side of the linkage is bonded to the nitrogen;
- R¹⁶, R¹⁷, and R¹⁸ are each independently H; C₁-C₃ alkyl; C₃-C₆ cycloalkyl; or phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- R¹⁹, R²⁰, R²¹, R²², R²³, and R²⁴ are each independently C₁-C₆ alkyl; C₂-C₆ alkenyl; C₁-C₄ alkoxy; or phenyl;
- each R²⁵ is independently C₁-C₄ alkyl; C₁-C₄ haloalkyl; C₂-C₄ alkenyl; C₁-C₄ alkoxy; or phenyl;
- m, n and p are each independently 0, 1 or 2;
- r is 0 or 1; and
- s is 2 or 3.
2. A compound of Claim 1 wherein:
- E is selected from the group 1*H*-pyrrole-1,2-, 2,3- and 3,4-diyl; 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl; 1*H*-pyrazole-1,5-, 3,4- and

- 4,5-diyl; 1*H*-imidazole-1,2-, 4,5- and 1,5-diyl; 3,4- and 4,5-isoxazolediyl;
 4,5-oxazolediyl; 3,4- and 4,5-isothiazolediyl; 4,5-thiazolediyl;
 1*H*-1,2,3-triazole-1,5- and 4,5-diyl; 2*H*-1,2,3-triazole-4,5-diyl;
 1*H*-1,2,4-triazole-1,5-diyl; 4*H*-1,2,4-triazole-3,4-diyl;
 5 1,2,3-oxadiazole-4,5-diyl; 1,2,5-oxadiazole-3,4-diyl;
 1,2,3-thiadiazole-4,5-diyl; 1,2,5-thiadiazole-3,4-diyl; 1*H*-tetrazole-1,5-diyl;
 2,3- and 3,4-pyridinediyl; 3,4- and 4,5-pyridazinediyl; 4,5-pyrimidinediyl;
 2,3-pyrazinediyl; 1,2,3-triazine-4,5-diyl; 1,2,4-triazine-5,6-diyl;
 10 1*H*-indole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-,
 1,2-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-,
 2,3-, 4,5-, 5,6- and 6,7-benzofurandiyl; benzo[*b*]thiophene-2,4-, 2,5-, 2,6-,
 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 2,3-, 4,5-, 5,6- and 6,7-diyl; 1*H*-indazole-1,4-,
 1,5-, 1,6-, 1,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl;
 15 1*H*-benzimidazole-1,4-, 1,5-, 1,6-, 1,7-, 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and
 6,7-diyl; 1,2-benzisoxazole-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-,
 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and 6,7-benzoxazolediyl; 1,2-benzisothiazole-3,4-,
 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-diyl; 2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6- and
 6,7-benzothiazolediyl; 2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-,
 4,7-, 4,8-, 2,3-, 3,4-, 5,6-, 6,7- and 7,8-quinolinediyl; 1,5-, 1,6-, 1,7-, 1,8-,
 20 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-, 6,7- and
 7,8-isoquinolinediyl; 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-, 4,8-, 3,4-, 5,6-,
 6,7- and 7,8-cinnolinediyl; 1,5-, 1,6-, 1,7-, 1,8-, 5,6-, 6,7- and
 7,8-phthalazinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 4,5-, 4,6-, 4,7-, 4,8-, 5,6-, 6,7- and
 7,8-quinazolinediyl; 2,5-, 2,6-, 2,7-, 2,8-, 2,3-, 5,6-, 6,7- and
 25 7,8-quinoxalinediyl; 1,8-naphthyridine-2,5-, 2,6-, 2,7-, 3,5-, 3,6-, 4,5-, 2,3-
 and 3,4-diyl; 2,6-, 2,7-, 4,6-, 4,7-, 6,7-pteridinediyl;
 pyrazolo[5,1-*b*]thiazole-2,6-, 2,7-, 3,6-, 3,7-, 2,3- and 6,7-diyl;
 thiazolo[2,3-*c*]-1,2,4-triazole-2,5-, 2,6-, 5,6-diyl;
 2-oxo-1,3-benzodioxole-4,5- and 5,6-diyl; 1,3-dioxo-1*H*-isoindole-2,4-, 2,5-,
 30 4,5- and 5,6-diyl; 2-oxo-2*H*-1-benzopyran-3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-,
 4,7-, 4,8-, 5,6-, 6,7- and 7,8-diyl; [1,2,4]triazolo[1,5-*a*]pyridine-2,5-, 2,6-,
 2,7-, 2,8-, 5,6-, 6,7- and 7,8-diyl;
 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazine-3,5-, 3,6-, 3,7-, 3,8-, 5,6-, 6,7-
 and 7,8-diyl; 2,3-dihydro-2-oxo-3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and
 6,7-benzofurandiyl; thieno[3,2-*d*]thiazole-2,5-, 2,6-, and 5,6-diyl;
 35 5,6,7,8-tetrahydro-2,5-, 2,6-, 2,7-, 2,8-, 3,5-, 3,6-, 3,7-, 3,8-, 4,5-, 4,6-, 4,7-,

- 4,8-, 2,3- and 3,4-quinolinediyl;
 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazole-2,4-, 2,5-, 2,6-, 2,7-, 4,5-, 5,6-
 and 6,7-diyl; 1,3-benzodioxole-2,4-, 2,5-, 4,5- and 5,6-diyl; 2,3-dihydro-2,4-,
 2,5-, 2,6-, 2,7-, 3,4-, 3,5-, 3,6-, 3,7-, 4,5-, 5,6- and 6,7-benzofurandiyl;
 2,3-dihydro-1,4-benzodioxin-2,5-, 2,6-, 2,7-, 2,8-, 5,6- and 6,7-diyl;
 5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-2,4-, 2,5-, 2,6-, 2,7-, 2,8-,
 3,4-, 3,5-, 3,6-, 3,7-, 3,8-, and 2,3-diyl; and 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, 2,7-,
 1,2-, and 2,3-naphthalenediyl; each aromatic ring system optionally
 substituted with one of R³, R⁴, or both R³ and R⁴;
- W is O;
 R¹ is C₁-C₃ alkyl or C₁-C₃ haloalkyl;
 R² is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; or C₃-C₆ cycloalkyl;
 R³ and R⁴ are each independently halogen; cyano; nitro; C₁-C₆ alkyl; C₁-C₆
 haloalkyl; C₁-C₆ alkoxy; C₁-C₆ haloalkoxy; C₁-C₆ alkylthio; C₁-C₆
 alkylsulfonyl; C₂-C₆ alkylcarbonyl; C₂-C₆ alkoxy carbonyl;
 (C₁-C₄ alkyl)NHC(O); (C₁-C₄ alkyl)₂NC(O); benzoyl; or phenylsulfonyl;
 Y is -O-; -CH=CH-; -C≡C-; -CH₂O-; -OCH₂-; -CH₂S(O)_{*n*}-; -CH₂O-N=C(R⁷)-;
 -(R⁷)C=N-OCH(R¹⁵)-; -C(R⁷)=N-O-; -CH₂OC(O)NH-; -CH₂S-C(R⁷)=N-;
 -CH=CR⁶-C(=W¹)-A¹-; or a direct bond;
- R⁷ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ alkylthio; C₂-C₆
 alkenyl; C₂-C₆ alkynyl; C₃-C₆ cycloalkyl; halogen; or cyano; or
 when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is
 -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken
 together as -(CH₂)_{*i*}-J- such that J is attached to Z;
- Z is selected from the group C₁-C₁₀ alkyl; C₃-C₈ cycloalkyl; phenyl; naphthalenyl;
 anthracenyl; phenanthrenyl; 1*H*-pyrrolyl; furanyl; thienyl; 1*H*-pyrazolyl;
 1*H*-imidazolyl; isoxazolyl; oxazolyl; isothiazolyl; thiazolyl;
 1*H*-1,2,3-triazolyl; 2*H*-1,2,3-triazolyl; 1*H*-1,2,4-triazolyl; 4*H*-1,2,4-triazolyl;
 1,2,3-oxadiazolyl; 1,2,4-oxadiazolyl; 1,2,5-oxadiazolyl; 1,3,4-oxadiazolyl;
 1,2,3-thiadiazolyl; 1,2,4-thiadiazolyl; 1,2,5-thiadiazolyl; 1,3,4-thiadiazolyl;
 1*H*-tetrazolyl; 2*H*-tetrazolyl; pyridinyl; pyridazinyl; pyrimidinyl; pyrazinyl;
 1,3,5-triazinyl; 1,2,4-triazinyl; 1,2,4,5-tetrazinyl; 1*H*-indolyl; benzofuranyl;
 benzo[*b*]thiophenyl; 1*H*-indazolyl; 1*H*-benzimidazolyl; benzoxazolyl;
 benzothiazolyl; quinolinyl; isoquinolinyl; cinnolinyl; phthalazinyl;
 quinazolinyl; quinoxalinyl; 1,8-naphthyridinyl; pteridinyl;
 2,3-dihydro-1*H*-indenyl; 1,2,3,4-tetrahydronaphthalenyl;

- 6,7,8,9-tetrahydro-5*H*-benzocycloheptenyl;
 5,6,7,8,9,10-hexahydrobenzocyclooctenyl; 2,3-dihydro-3-oxobenzofuranyl;
 1,3-dihydro-1-oxoisobenzofuranyl; 2,3-dihydro-2-oxobenzofuranyl;
 3,4-dihydro-4-oxo-2*H*-1-benzopyranyl;
 5 3,4-dihydro-1-oxo-1*H*-2-benzopyranyl;
 3,4-dihydro-3-oxo-1*H*-2-benzopyranyl;
 3,4-dihydro-2-oxo-2*H*-1-benzopyranyl; 4-oxo-4*H*-1-benzopyranyl;
 2-oxo-2*H*-1-benzopyranyl; 2,3,4,5-tetrahydro-5-oxo-1-benzoxepinyl;
 2,3,4,5-tetrahydro-2-oxo-1-benzoxepinyl;
 10 2,3-dihydro-1,3-dioxo-1*H*-isoindolyl;
 1,2,3,4-tetrahydro-1,3-dioxoisoquinolyl;
 3,4-dihydro-2,4-dioxo-2*H*-1,3-benzoxazinyl; 2-oxo-1,3-benzodioxyl;
 2,3-dihydro-1,1,3-trioxo-1,2-benzisothiazolyl; 9*H*-fluorenyl; azulenyl; and
 thiazolo[2,3-*c*]-1,2,4-triazolyl; each group substituted with R⁹ and optionally
 15 substituted with one or more R¹⁰;
 R⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆
 haloalkoxy; C₁-C₆ alkylthio; cyano; CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl);
 N(C₁-C₆ alkyl)₂; SiR²²R²³R²⁴; or GeR²²R²³R²⁴; or R⁹ is C₃-C₆ cycloalkyl,
 phenyl, phenoxy, pyridinyl, pyridinyloxy, pyrimidinyl, or pyrimidinyloxy, each
 20 optionally substituted with one of R¹¹, R¹², or both R¹¹ and R¹²; and
 each R¹⁵ is independently H; C₁-C₃ alkyl; or C₃-C₆ cycloalkyl.
3. A compound of Claim 2 wherein:
 E is selected from the group 2,3- and 3,4-furandiyl; 2,3- and 3,4-thiophenediyl;
 2,3- and 3,4-pyridinediyl; 4,5-pyrimidinediyl; 2,4-, 2,7-, 3,5-, 2,3-, 4,5-, 5,6-
 25 and 6,7-benzofurandiyl; benzo[*b*]thiophene-2,4-, 2,7-, 3,5-, 2,3-, 4,5-, 5,6-
 and 6,7-diyl; and 1,6-, 1,7-, 1,2-, and 2,3-naphthalenediyl; each aromatic ring
 system optionally substituted with one of R³, R⁴, or both R³ and R⁴;
 Z is selected from the group phenyl; 1,2,4-thiadiazolyl; pyridinyl; pyrimidinyl; and
 naphthalenyl; each group substituted with R⁹ and optionally substituted with
 30 one or more R¹⁰;
 R⁷ is H; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy; C₁-C₆ alkylthio; C₂-C₆
 alkenyl; C₂-C₆ alkynyl; cyclopropyl; halogen; or cyano; or
 when Y and an R¹⁰ are attached to adjacent atoms on Z and Y is
 -CH₂O-N=C(R⁷)-, R⁷ and said adjacently attached R¹⁰ can be taken
 35 together as -(CH₂)_{*f*}-J- such that J is attached to Z;
 J is -CH₂- or -CH₂CH₂-; and

r is 1.

4. A compound of Claim 3 wherein:

A is O; N; NR⁵; or CR¹⁴;

X is OR¹;

5 R¹ is C₁-C₃ alkyl;

R² is H or C₁-C₂ alkyl;

Y is -O-; -CH=CH-; -CH₂O-; -CH₂O-N=C(R⁷)-; -(R⁷)C=N-OCH(R¹⁵)-;
-CH₂OC(=O)NH-; -CH₂S-C(R⁷)=N-; or -CH=CR⁶-C(=W¹)-A¹-;

10 R⁷ is H; C₁-C₃ alkyl; C₁-C₃ haloalkyl; C₁-C₃ alkoxy; C₁-C₃ alkylthio; or cyclopropyl; and

each R¹⁵ is independently H; C₁-C₃ alkyl; or cyclopropyl.

5. A compound of Claim 4 wherein:

A is O or NR⁵;

G is C; and

15 Y is -O-; -CH₂O-; or -CH₂O-N=C(R⁷)-.

6. A compound of Claim 5 wherein:

R¹ is methyl; and

R² is methyl.

7. A compound of Claim 4 wherein:

20 A is N or CR¹⁴;

G is N; and

Y is -O-; -CH₂O-; or -CH₂O-N=C(R⁷)-.

8. A compound of Claim 7 wherein:

R¹ is methyl; and

25 R² is methyl.

9. The compound of Claim 4 which is selected from the group:

2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trimethylsilyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3H-1,2,4-triazol-3-one;

30 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]-3-thienyl]-3H-1,2,4-triazol-3-one;

4-[2-[(2,5-dimethylphenoxy)methyl]-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one;

35 (1,1-dimethylethyl) 2-chloro-3-[3-(1,5-dihydro-3-methoxy-1-methyl-5-oxo-4H-1,2,4-triazol-4-yl)-2-thienyl]-2-propenoate;

4-[2-[[[3-(4-chlorophenyl)-1,2,4-thiadiazol-5-yl]oxy]methyl]-3-thienyl]-2,4-dihydro-5-methoxy-2-methyl-3*H*-1,2,4-triazol-3-one; and
2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[3-[4-(trifluoromethyl)phenyl]-1,2,4-thiadiazol-5-yl]oxy]methyl]-3-thienyl]-3*H*-1,2,4-triazol-3-one.

- 5 10. A fungicidal composition comprising a fungicidally effective amount of a compound of Claim 1 and at least one of a surfactant, a solid diluent or a liquid diluent.

11. A method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of a compound of Claim 1.

10

INTERNATIONAL SEARCH REPORT

In ☐ national Application No
PCT/US 96/06533

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D405/04 A01N43/647 C07D409/04 C07D401/04 C07D249/12
C07D261/12 C07D413/04 C07D417/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 14009 (DU PONT DE NEMOURS) 26 May 1995 * see claim 1 and Tables 11 and 12 *	1-11
Y	DE,A,41 02 339 (BAYER) 30 July 1992 see page 20, line 43 - page 21, line 5; claim 1	1-11
Y	DE,A,41 18 720 (BAYER) 10 December 1992 see page 14, line 1-2	1-11
Y	EP,A,0 554 956 (ISAGRO) 11 August 1993 see page 4-5; claim 1	1-11
A	WO,A,92 16510 (CIBA-GEIGY) 1 October 1992 see page 24-27; claim 1	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- * "&" document member of the same patent family

Date of the actual completion of the international search

6 August 1996

Date of mailing of the international search report

23. 08.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Lauro, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/US 96/06533

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9514009	26-05-95	AU-B- 7953594	06-06-95
DE-A-4102339	30-07-92	DE-D- 59206587	25-07-96
		EP-A- 0497127	05-08-92
		JP-A- 5078314	30-03-93
		US-A- 5350861	27-09-94
DE-A-4118720	10-12-92	AU-B- 1732692	10-12-92
		CA-A- 2070717	08-12-92
		EP-A- 0517052	09-12-92
		JP-A- 5194493	03-08-93
		US-A- 5244865	14-09-93
EP-A-554956	11-08-93	IT-B- 1254199	14-09-95
		JP-A- 6293757	21-10-94
		US-A- 5334605	02-08-94
WO-A-9216510	01-10-92	AT-T- 139768	15-07-96
		AU-B- 1343192	21-10-92
		BR-A- 9205752	08-11-94
		CA-A- 2106302	20-09-92
		CN-A- 1064862	30-09-92
		DE-D- 69211841	01-08-96
		EP-A- 0577629	12-01-94
		JP-T- 6506201	14-07-94
		NZ-A- 241996	25-11-94
		SI-A- 9210249	30-04-95
		TR-A- 25475	01-05-93
		US-A- 5506193	09-04-96
		US-A- 5494890	27-02-96